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THE UNIVERSITY OF ALBERTA

THE SOLVENT EXTRACTION OF MOLYBDENUM FROM WET-PROCESS INDUSTRIAL PHOSPHORIC ACID

by

© PETER J. GRIFFIN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE

IN

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DEPARTMENT OF MINERAL ENGINEERING

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THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled "The Solvent Extraction of Molybdenum From Wet-Process Industrial Phosphoric Acid", submitted by Peter J. Griffin, in partial fulfilment of the requirements for the degree of Master of Science in Metallurgy.

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ABSTRACT

Many phosphate fertilizers are manufactured in North America by dissolving phosphate rock in sulphuric acid to yield a phosphoric acid filtrate ($\sim$28% P_2O_5). After concentrating the acid by evaporation (>40% P_2O_5), it is neutralized with anhydrous ammonia in a saturator to precipitate ammonium phosphate fertilizer. The raw feed and subsequent fertilizer contain several valuable metals including zinc, chromium, vanadium, manganese, molybdenum, cobalt, copper, nickel and cadmium, many of which do not serve as soil micro-nutrients thereby not enhancing the effectiveness of the fertilizer.

To investigate the possible recovery of these metals as by-products, solvent extraction of molybdenum from phosphoric acid was examined with a range of organic extractants. At present, only uranium is extracted industrially, by liquid ion exchange, from the intermediate stage 5-6M process acid. The optimum solvent for molybdenum extraction was a combination of two liquid amine-type extractants, alamine 336 (12%), and tributylamine (10%), plus a long chain alcohol, decanol (15%), dissolved in kerosene. The effects of varying amine concentration, diluent, temperature, molybdenum concentration, acid molarity and mixing time were studied. Interference

from other metal species was examined, and a possible reaction equation suggested.

The metals were extracted from an industrially produced acid by the optimum extractant in a three-stage countercurrent process. About 85% of the molybdenum was removed, along with varying amounts of the other metals. The effect of pH on stripping was examined and suggestions made for scrubbing, stripping and further processing to ammonium paramolybdate.

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BACKGROUND

Introduction

The ever increasing demand for metals, with its associated economic and environmental implications, has stimulated much interest in by-product recovery. The phosphate rock industry has many advantages for by-product production. It processes large volumes with valuable constituents in solution, which are incidental in the final product. Uranium has been extracted for several years from an intermediate aqueous acid solution produced in the process. As the acid also contains many other metals it is worthwhile investigating the extraction of other constituents.

Any metal must be extracted from the acid without substantially changing the character of the acid on its route to fertilizer production. Therefore, precipitation of a metal by acidity change is prohibited, electrowinning would be difficult with the low metal and high acid concentration. Ion-exchange and solvent extraction would be possible, but the former has few exchangers that would not be poisoned by one of the wide range of metals present in the industrial acid. Solvent extraction, although limited in the number of extractants suitable for high acid

concentrations, is preferred to ion-exchange industrially by virtue of lower capital cost and wider range of industrial extractants.

Therefore the general goal of this study is to remove a metal as a by-product from an intermediate step in phosphate rock processing by solvent extraction.

Solvent Extraction

Solvent extraction, in the mineral industry, is the transfer of an inorganic species, generally an ionic metallic species, between an aqueous and an organic solution. The organic phase consists of an *extractant*, a *modifier* and a *diluent*, all immiscible with water. The diluent forms the bulk of the organic phase, it does not participate in the metal extraction but is used to carry the small quantity of active extractant. The extractant is the active component which forms some type of chemical bond with the metallic species. The modifier alters the properties of the organic phase, either by changing the viscosity or by combining with the extractant to make it miscible with the kerosene.

The general industrial route starts with a moderately acidic or basic process stream containing several metal species. The aqueous stream flows through a

set of mixer tanks and settling tanks counter currently to the organic stream. Each mixing of organic and aqueous phases is a *contact*; 3 contacts would be a 3 *stage* process.

Some of the metals will be preferentially transferred to the organic phase. The *loaded* organic phase may have extracted some waste metals which can be removed by *scrubbing*, normally with a neutral solution. The valuable metal will be removed from the organic phase by *stripping* with a pure acidic or basic solution in a multistage process. The cleaned organic is recycled to process a fresh industrial stream.

The advantages of solvent extraction are:

i) the extractant can be recycled with little loss of extractant by entrainment in the aqueous phase.

ii) the required metal may be selectively extracted from the aqueous solution.

iii) the required metal may be concentrated if the *phase ratio* between organic and aqueous phases in the stripping process is less than one.

The major disadvantages are the lack of treatment routes for strongly acidic or basic solutions and the low number of extractants available in industrially required volumes at a reasonable cost. Economically solvent

extraction is most viable for large volume process streams, or for processing high value metals, e.g., copper leaching, U, Zr, Hf.

The effectiveness of a solvent extraction process can be measured by three variables;

$$\text{percentage extraction, } E_x \equiv \frac{\text{mass of x extracted}}{\text{mass of x in feed}},$$

$$\text{extraction coefficient, } D_x \equiv \frac{\text{conc. of x in organic}}{\text{conc. of x in feed}}$$

and selectivity coefficient of x over y, $S_x^y \equiv \frac{D_x}{D_y}$.

Industrial organic extractants fall into principally four different groupings; solvating reagents, liquid cation exchangers, liquid anion exchangers, and hydroxime reagents. Examples of each type and the mechanisms of extraction are included with details of all extractants used in this research in Appendix I. *Synergistic* extraction occurs when a mixture of two extractants will perform better than either one individually.

Solvent extraction is used for a wide range of industrial operations. Table I details the conditions of some well established operations and their approximate costs. Marcus and Kertes[1] have presented a detailed study of most aspects of the theory of solvent extraction and several books are available which review the industrial aspects.

Table I - Industrial Applications of Solvent Extraction

Extracted Species	Feed Conc. g/l	Aqueous System	Organic System	Phase Ratio, A/O	cost per lb of metal
Cu	Cu 3	4.5g/l H_2SO_4	8% LIX-64N	1/2	10¢
U	U 0.3	H_2SO_4	5% Alamine 336	15/1	40¢
U	U 400	3M HNO_3	30% TBP	1/1	
Ta-Nb			MIBK		
Cu-Co-Ni	Ni 118 Co 2 Cu 2	160g/l HCl	11% TOA	1/1	
Zr-Hf	Zr 100 Hf 2	1M HCl 3M HCNS	MIBK	1/2	$1.25
H_3PO_4	H_3PO_4 100	50g/l HCl	Iso-amyl alcohol		40¢
Br_2		sea water	CCl_4		
Rare Earths	Y 0.1	H_2SO_4 pH 1.5	5% Alamine 336	20/1	$1.70
Co-Ni	Co 20 Ni 9	H_2SO_4 pH 5-6	30% DEHPA	1/1	13¢
Zr-Hf	Zr 95 Hf 1.5	7.5N HNO_3	50% TBP	1/3	80¢

Phosphate Rock Industry

Industrial phosphoric acid is produced as an intermediate product in the manufacture of phosphate fertilizers from phosphate rock. In 1976, North American companies produced over 44 million metric tons of phosphate rock, representing over 40% of the world production. Other major sources are Morocco, China and the USSR producing a world total of 111 million tons. The bulk of the rock is mined in Florida and North Carolina, with small quantities also produced in Tennesee and the mid-West states. About 25% of the rock is exported, 3.5 million tpa to Canada, where it is generally used by companies which have a surfeit of sulphuric acid and/or ammonia in their operations.

Fertilizer Production:

Typically, phosphate rock is mined in a cut 350 ft wide, 40 ft deep and 3000 ft long by drag lines. The rock matrix is turned into a slurry with high pressure water guns and pumped to the beneficiation plant. Hoppe[2,3] gives a detailed report on the mining and processing of phosphate rock in Florida. His detailed process diagrams are reproduced in Appendix II.

The raw rock, 25% BPL (bone phosphate of lime

$Ca_3(PO_4)_2$), is washed and classified, producing + 6-mesh, and 6 to 16 mesh products. The 16 to 35 mesh fraction is beneficiated by cyclones and classifiers, the 35 to 150 mesh fraction by flotation. The final rock product is about 75% BPL and 60% -200 mesh. The phosphate rock is digested in sulphuric acid, producing an impure gypsum slurry and phosphoric acid. If the rock was calcined to remove organic material 'green acid' is produced, otherwise 'brown acid' is formed. This wet process acid, 30% P_2O_5, is used for the solvent extraction operation.

The wet process acid is normally evaporated to 54% P_2O_5, with hydrofluorosilicic acid being recovered from the fumes. The concentrated acid is then either reacted with phosphate rock and dried to form triple superphosphate, or reacted with ammonia and dried to form granular ammoniated phosphates. Table II shows the composition of various phosphate rocks and products. Canada has 10 phosphoric acid plants producing 2.5 million tons of P_2O_5 equivalent annually.

Acid Composition:

The wet process acid contains numerous metals in varying concentrations. Typical compositions are shown in

Table II - Typical phosphate rock and fertilizer composition

%	Florida Rock	Idaho Rock	Morocco Rock	Florida normal super phosphate	Florida conc. super phosphate
P_2O_5	33	31.6	35.1	20	48
CaO	48	47	53	29.5	20
MgO	0.35	0.7	0.2	0.1	0.4
F	3.7	3.6	1.6	1.7	2
CO_2	3.3	2.5	4.1	0.1	0.1
SO_3	0.9	1.7	1.4	29	3.4
SiO_2	5.5	5.5	0.9	4.4	4.4
K_2O	0.1	0.37	0.2		
Na_2O	0.5	0.6	1.2	0.11	
Fe_2O_3		0.9	0.1		
Al_2O_3		1.5	0.4	0.7	1.4
U_2O_5		0.25		0.7	1.9

Table III, with the estimated annual North American metal loss. Only some of the metals are plant micronutrients; these may only partially, or not at all, be required as additions to the soil.

Table III - Typical metal concentrations in North American wet process acids and associated annual losses

Metal	Concentration g/l		Estimated Loss
	Average	Range	tpa
Al	variable	2-25	
Fe*	8	4.5-15	
Mg	4	2-6	
Na	4	0.01-5	
K*	variable	0.1-0.4	
Mn*	0.1	0.01-1.5	
Cu*	0.002	0.01-0.9	
Zn*	0.08	0.01-5	700-2000
Ni*	0.05	0.02-0.1	
Cr	0.5	0.01-1.4	3000-9000
Mo*	0.05	0.01-0.08	400-800
As_2O_3	variable	0.02-1.6	
U	0.14	0.05-2	2500-2700
V	0.1	0.1-0.3	700-1500
Ca	2-4	0.1-5	
Ti	0.1-0.3	0.1-5	
Ag	-	∿ .02	
Se	-	0.001-0.006	
Co	-	0.001-0.003	

*micronutrient

It has been estimated[4] that 2500 - 2700 metric tons of U_3O_8 are annually lost in the acid and about 0.5 million metric tons of U_3O_8 are contained in U.S. mineable phosphate reserves. As acid composition varies it is difficult to estimate Canadian wastage but it would be about 11% of the American loss in Table II.

Solvent Extraction from Phosphoric Acid

In the late 1940's, with uranium in great demand, phosphoric acid was recognized as a readily available source of uranium. Eventually three commercial operations[5] came into production, two using a solvent extraction technique with a pyrophosphate ester[6] and the third plant using a chemical preparation method. The effect of various extractants became well documented[7], but the development of other uranium supplies made the phosphoric acid route redundant within a few years. The recent upsurge in uranium prices from $10 to $50 per lb U_3O_8 led to the development of new processes.

Oak Ridge Laboratory developed the first process[8,9] using a mixture of di-2ethylhexylphosphoric acid (DEHPA) and trioctylphosphine oxide (TOPO) as the extractant; the two cycle process is shown in Fig. 1. Iron is added to the first extraction cycle strip solution to reduce the uranium to the less extractable tetravalent state.

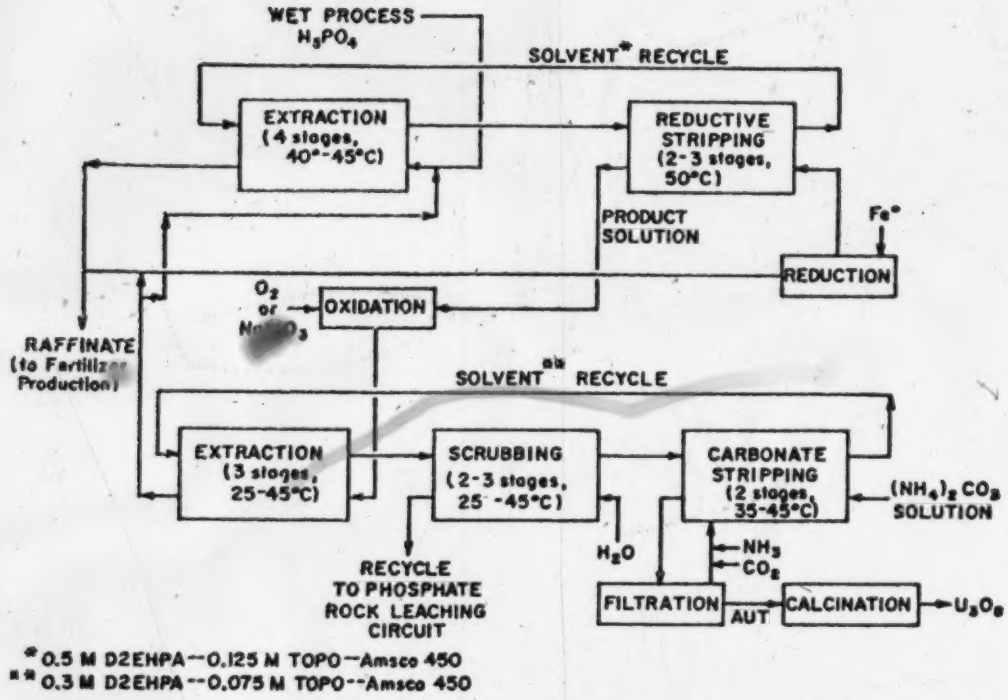


Figure 1 - Process for the recovery of uranium from wet-process phosphoric acid.[8]

The wet process acid solution must be oxidized to return uranium to the preferred hexavalent state. The higher temperature in the stripping stages is to increase stripping efficiency. The uranium is precipitated with ammonia to produce an ammonium uranyl tricarbonate slurry which is 97% uranium after calcination. A further development[10] used a different type of extractant in the first cycle, octylphenylphosphoric acid (OPPA). The stripping is carried out with the concentrated process acid (54% P_2O_5), which also contains sodium chlorate. The oxidizing agent forms a hexavalent uranium ion which is less extractable than the tetravalent ion for OPPA extractant; the reverse is true for the DEHPA-TOPO extractant. Hurst[11] has reported favorably on the economics of these processes.

Ross[4] reports the present state-of-the-art and gives a brief outline of the Uranium Recovery Corporation (URC) modular extraction and central processing plant. URC have installed 4 extraction modules in Florida, capable of producing 1.3 million lb of uranium per year. Westinghouse, Gulf Oil Chemicals and Freeport Minerals are also involved in pilot plant operations in the Florida region. McGinley[12] has estimated that 2000-3000 tons of U_3O_8 could be produced annually at a cost of $10 or less per lb, representing 20% of the current North American

demand. Working operations and those under construction have a total capacity of 650 tons of U_3O_8 in 1977.

The extraction of uranium from Mexican phosphate deposits has been reported[13], and a patent has been issued for the extraction of uranium and heavy metals in Japan[14].

The solvent extraction of vanadium from phosphoric acid has been reported in a series of patents assigned to Kerr-McGee Chemical Corporation. The patents suggest extracting vanadium with α-hydroxyoximes[15], fluorinated β-diketones[16], organophosphates[17], amines[18], and phosphine oxides[19].

The following references complete the study of the removal of metals from phosphate solutions. The U.S. Bureau of Mines examined the waste solution and sludge from the phosphate coating of steel. The first investigation[20] involved a liquid extractant, dinonyl naphthalene sulfonic acid (DNSA) and DEHPA, capable of recovering nickel and zinc from solution. A second report[21] demonstrated a laboratory scale process for recovering zinc and iron with DEHPA and isopropyl ether, respectively. These techniques are not suitable for wet process acid, as the phosphate concentration is only 3.8 g/l and the pH 3-4.

Arsenic impurities have been reported to be

removed from phosphoric acid by solvent extraction[22]. Cadmium, copper and arsenic can be removed as sulphides from the acid by treatment with sodium sulphide under pressure[23]. Solvent extraction can also be used to purify phosphoric acid by the extraction of the acid only into the organic phase. Raz[24] reports on the first full scale plant which can produce high-grade detergents, technical products and liquid fertilizer, in addition to the normal range of phosphatic fertilizers.

Aim and Scope

Any possible process for removing metals from phosphoric acid has the advantage of receiving the metals in solution, so no digesting costs are involved. The disadvantage is that after extraction of the metals the solution must be relatively unchanged in character.

The aim of the research, taking into account the present situation in the phosphate industry, is to remove moderately valuable metals, other than uranium, from the wet process acid. If possible the removal must be carried out by an economically viable route, allowing the resultant acid stream to continue to the manufacture of phosphate fertilizers.

The scope of the research was limited to studying

the use of solvent extraction techniques for the removal of the metals, concentrating primarily on industrial extractants. The effect of changing the organic extractants, varying the chemical composition of the aqueous solution and using industrial wet process acids were studied.

EXPERIMENTAL

Preparation of Chemicals

Three types of solution were used in the solvent extraction experiments, two aqueous and one organic. The primary aqueous solution, 30% P_2O_5, was made artificially using Matheson, Coleman and Bell 85% phosphoric acid diluted with water to the required concentration. The required metal concentrations were produced by additions of concentrated solutions of the various metals: $VOSO_4 \cdot 2\ H_2O$ soln., $(NH_4)_6Mo_7O_{24} \cdot 4\ H_2O$ soln., $UO_2(NO_3)_2 \cdot 6\ H_2O$ soln., K_2CrO_4 soln., Fe in HNO_3, Ni in HNO_3 and Zn in HCl.

The second aqueous solution was industrial 'brown' wet process phosphoric acid supplied by Sherritt Gordon Mines Limited, with the metal content shown in Table IV.

Table IV - Sherritt Gordon industrial acid

P_2O_5	28%
Mo	51.4 ppm
V	104 ppm
Cr	678 ppm
Ni	42.3 ppm
Zn	89.5 ppm
Fe	8.01 g/l
U	< 50 ppm

The organic extractant solutions were made up by volume percentage of the extractant in kerosene. Appendix I gives the industrial names, chemical formulae and some properties of the extractants used in the research.

Details of the aqueous and organic phase composition, in addition to the extraction conditions for each test, are given in Appendix III.

Extraction

The extraction was carried out by placing 25 ml portions of organic and aqueous phases in 250 ml stoppered conical flasks. Mixing was carried out on a Blue M Company automatic water bath-shaker with an oscillation rate of 180/min and a displacement of 1 inch. Shaking time and temperature were varied as required, the bulk of the tests being carried out at room temperature with mixing for 10 min. The mixed phases were allowed to part in separatory funnels and the aqueous solution analysed.

Analysis

The analysis of the metals in the aqueous phase is complicated by the high concentration of phosphate ions. The analytical technique consists of three steps.

I. Vanadium, molybdenum, zinc, nickel, chromium and uranium were examined by atomic absorption using metal standards in a 30% P_2O_5 medium. Iron was analysed by X-ray fluorescence with similar standards. The conditions for each analysis are shown in Table V.

Table V - Analyses Conditions

Metal	Flame			Absorption Wavelength
	Air l/min	Acetylene cc/min 10^3	No l/min	nm
Ni	5	1.2	-	232.0
Zn	5	1.2	-	213.9
V	-	3.8	4.5	318.3
Mo	-	3.8	4.5	313.3
Cr	5	1.8	-	357.9
U	-	3.8	4.5	351.5
Cu	5	1.2	-	324.8

Fe 57.60° angle, LiF crystal

Cr tube at 32 kV, 16 mA.

The results of these analyses are 'raw' concentrations.

II. Phosphate ions interfere with the above analyses, so that solutions with a constant metal concentration will vary in apparent composition, if the phosphate concentration varies. The phosphate concentration will vary as some phosphoric acid may be removed by the organic extractant. If a small metal addition is made to the acid solution, the absorption of that species will be dependent on the phosphate concentration.

After the first series of analyses, a small copper solution additon was made to give a 10 ppm copper concentration. The absorption of the copper was determined and the phosphate concentration found from calibration curves.

III. The interference effect also occurs with the other metals so that after phosphate determination, the metal concentration must be changed to account for the phosphate interference. Calibration curves, Figure 2, show that with the 30% P_2O_5 as the standard, each 1% decrease in P_2O_5 concentration produced an "apparent" 4% increase in metal concentration; iron was the exception with only a 2% increase. Thus the true metal and phosphate concentrations can be found.

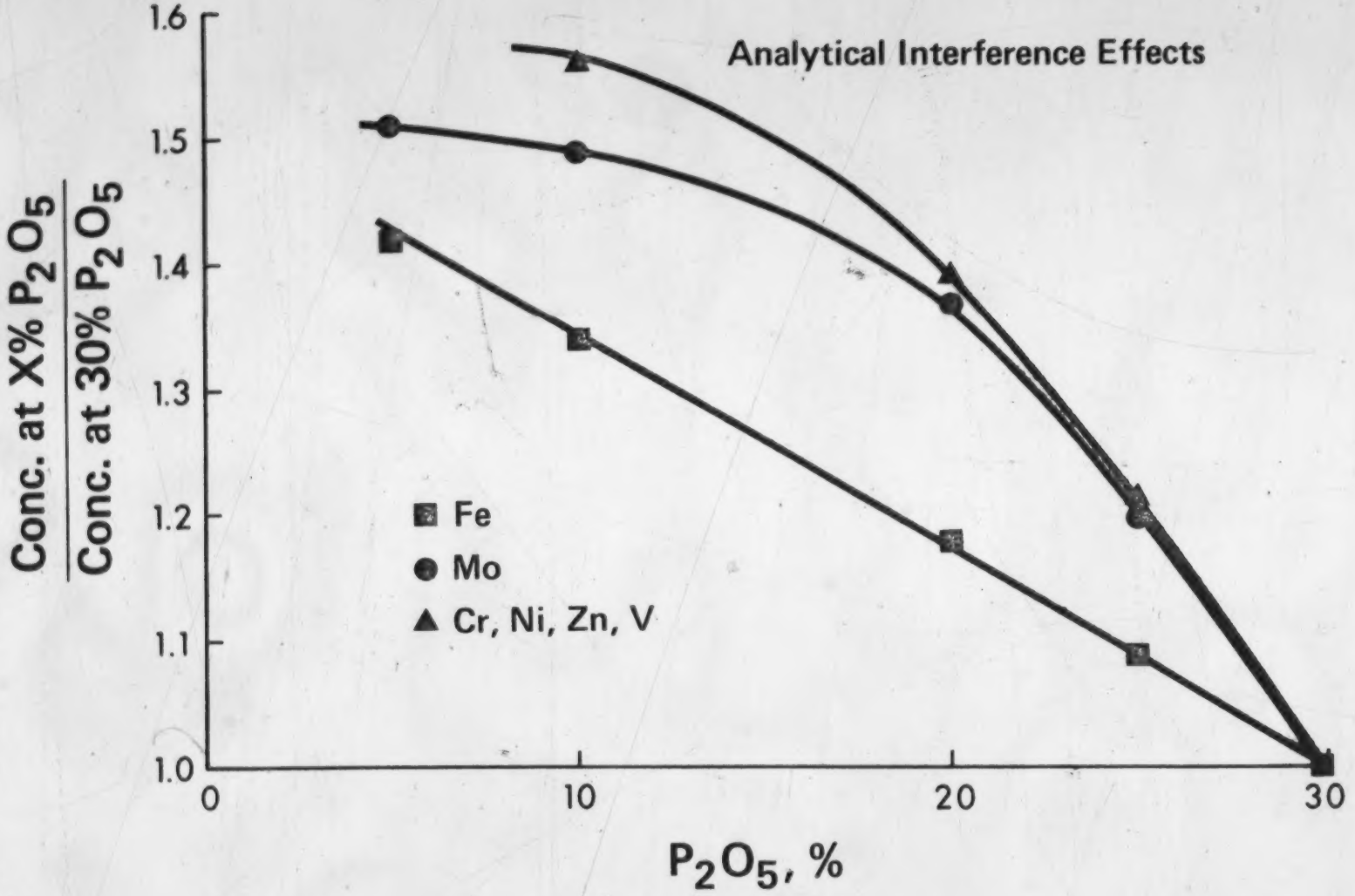


Figure 2 - Effect of P_2O_5 concentration on the analysis of metals in phosphoric acid.

COMPOSITION OF ORGANIC PHASE

The first aim was to extract a moderately valuable metal from the wet process acid using an industrially available liquid extractant. Ten industrial extractants were considered initially and contacted in a single stage with an acid solution containing molybdenum and vanadium.

Optimum Extractant Composition

The first results are reported in Table VI.

Table VI - Molybdenum and vanadium extraction with commercially available organic extractants

Organic Extractant	% Extraction		Phases
	molybdenum	vanadium	
Amberlite LA1	27	2	3
Amberlite LA2	20	2	3
Alamine 336	52	0	3
Aliquat 336	18	0	3
TOPO	27	0	2
Primene JMT	ppt	ppt	-
TBP	18	5	2
Octylamine	30	12	2
LIX 70	0	-	2
DEHPA	0	4	2
Triisoctylamine	35	0	3

All the organic solutions were 10% in kerosene. The artificial acid solution contained 30% P_2O_5, 50 ppm molybdenum and 200 ppm vanadium. All the following results use these specifications unless mentioned.

Obviously the combination of molybdenum extraction with alamine is the most promising - 52% Mo extraction. But the organic phase separates into two phases, a large upper phase and a small denser lower phase with a phase ratio of 1.86:1. Talät-Erben[25] suggested that the third phase is formed when the dipole moment and polarizability of extractant and diluent differ considerably. The denser organic phase appears to be a concentrated organic-molybdenum-phosphate agglomeration[26] which can accept increasing amounts of molybdenum. The lighter phase (mainly kerosene) contains little extractant, removing 15-30% of the molybdenum when the phase is formed and not extracting any further molybdenum.

Generally aromatic diluents do not form a two phase organic, possibly due to some Π-electron stabilization[26]. However, benzene and toluene, as well as chloroform and cyclohexane all reacted with the acid to form a solid.

Decanol in the extractant prevents third phase formation. The long chain alcohol forms hydrogen bonds with

the negatively-charged phosphate oxygen atoms, reducing the polarization and allowing mixing with the kerosene.

In one try to improve the molybdenum extraction, a range of non-industrial extractants similar to alamine were tried. Also, in an attempt to find a synergistic combination, alamine was combined with a wide variety of extractants; the results are shown in Table VII. Appendix I contains details of the organic extractants.

Within the limitations of the extractants examined, the combinations of alamine with tributylamine (TBA) and with dipropylamine (DPA) are the most effective with 68.6% and 64.0% Mo extraction, respectively. Figure 3 shows the variation in molybdenum extraction and phase formation for the best synergistic combinations, with increasing decanol concentration. The highest extraction is with the alamine/TBA combination which also separates into the normal two phases with over 15% decanol. The lack of three phases, compared with the DPA/alamine extractant, is due to the 3 butyl chains having a greater depolarization effect than two propyl groups, thus requiring less decanol to produce miscible phases.

With a decanol concentration of 15%, the concentration of the extractants was varied individually. The results are shown in Figures 4 and 5. Normally, the

Table VII - Molybdenum extraction with non-industrial extractants and extractant combinations.

Organic Extractant	Mo Extraction, %	Phases
6% alamine 4% aliquat	29.9	3
6% alamine 4% JMT	34.4	3
6% alamine 4% LA1	35.7	3
6% alamine 4% LA2	33.2	3
6% alamine 4% TBP	single phase	-
6% alamine 4% TOA	38.2	3
6% alamine 4% DEHPA	18.1	2
6% alamine 4% Oct.	44.8	3
6% alamine 4% TOPO	single phase	-
10% didodecylamine	single phase	-
10% di-n-propylamine	45.8	2
10% tri-n-butylamine	52.6	2
10% di-n-hexylamine	33.2	2
10% di-2-ethylhexylamine	ppt	-
10% hexylamine	46.6	2
10% n-decylamine	ppt	-
10% alamine 10% DPA	64.0	3
10% alamine 10% TBA	68.8	3
10% alamine 10% DHA	56.0	3
10% alamine 10% Hex.	60.6	3
10% alamine 10% DEHA	ppt	-

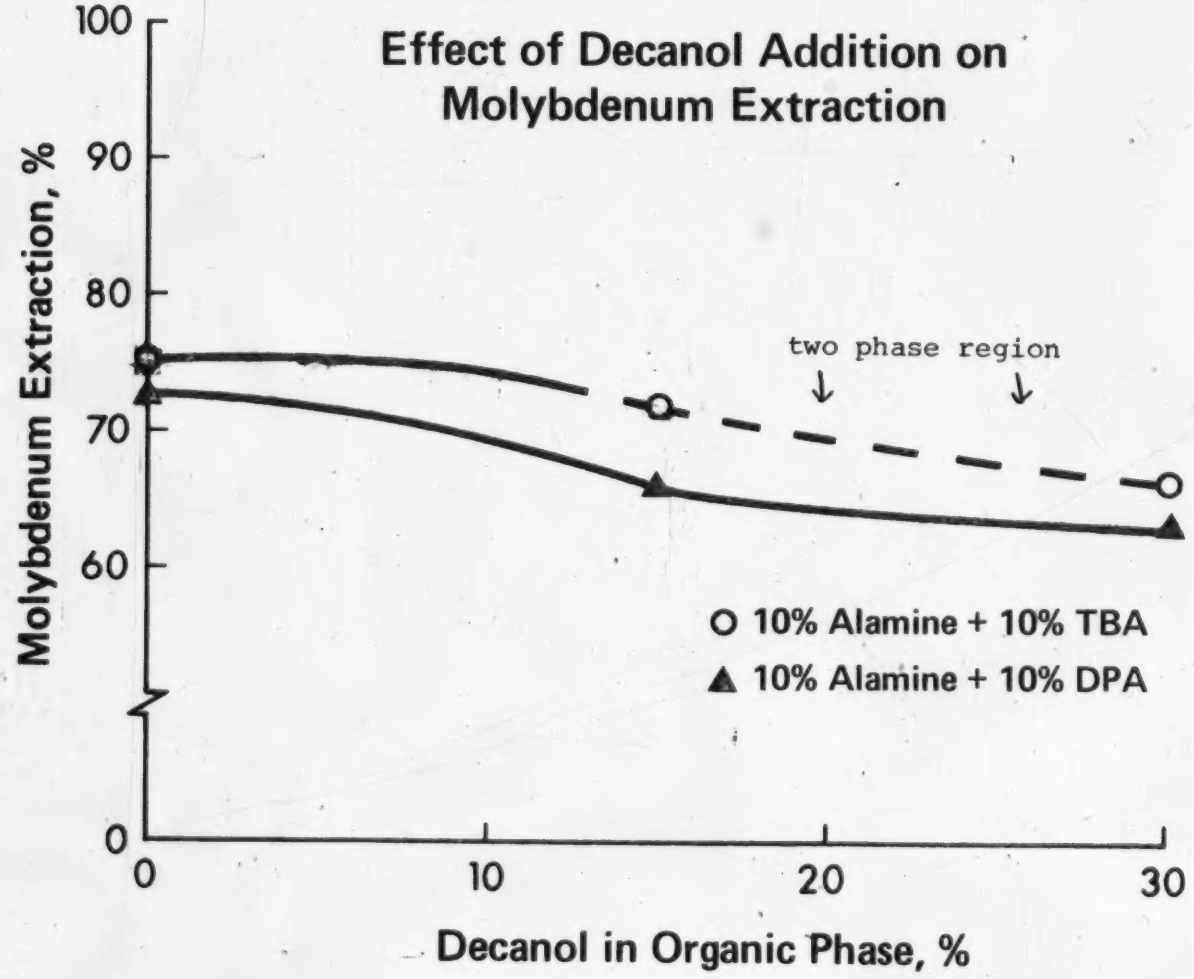


Figure 3 - Effect of decanol concentration on the extraction of molybdenum from alamine/TBA and alamine/DPA systems.

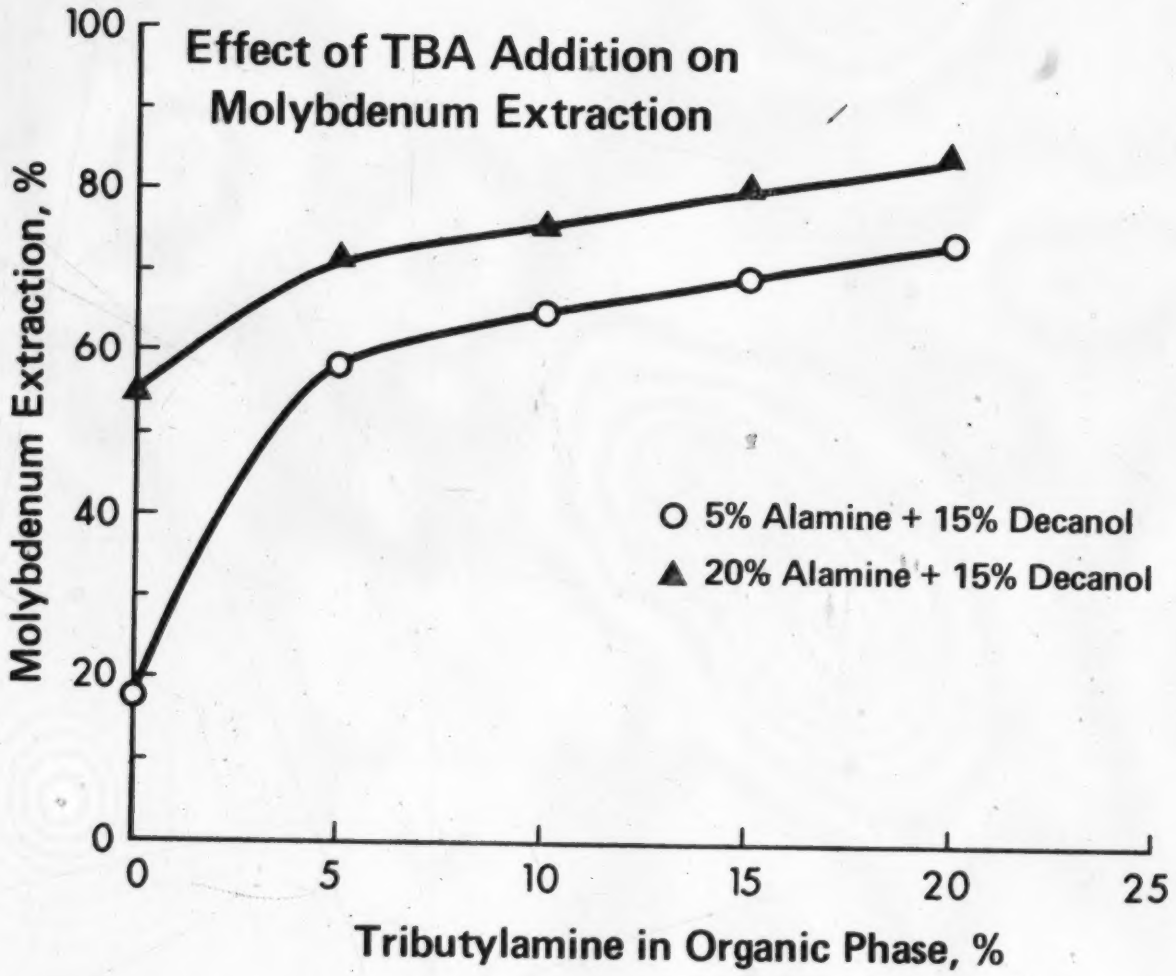


Figure 4 - Dependence of molybdenum extraction on TBA concentration.

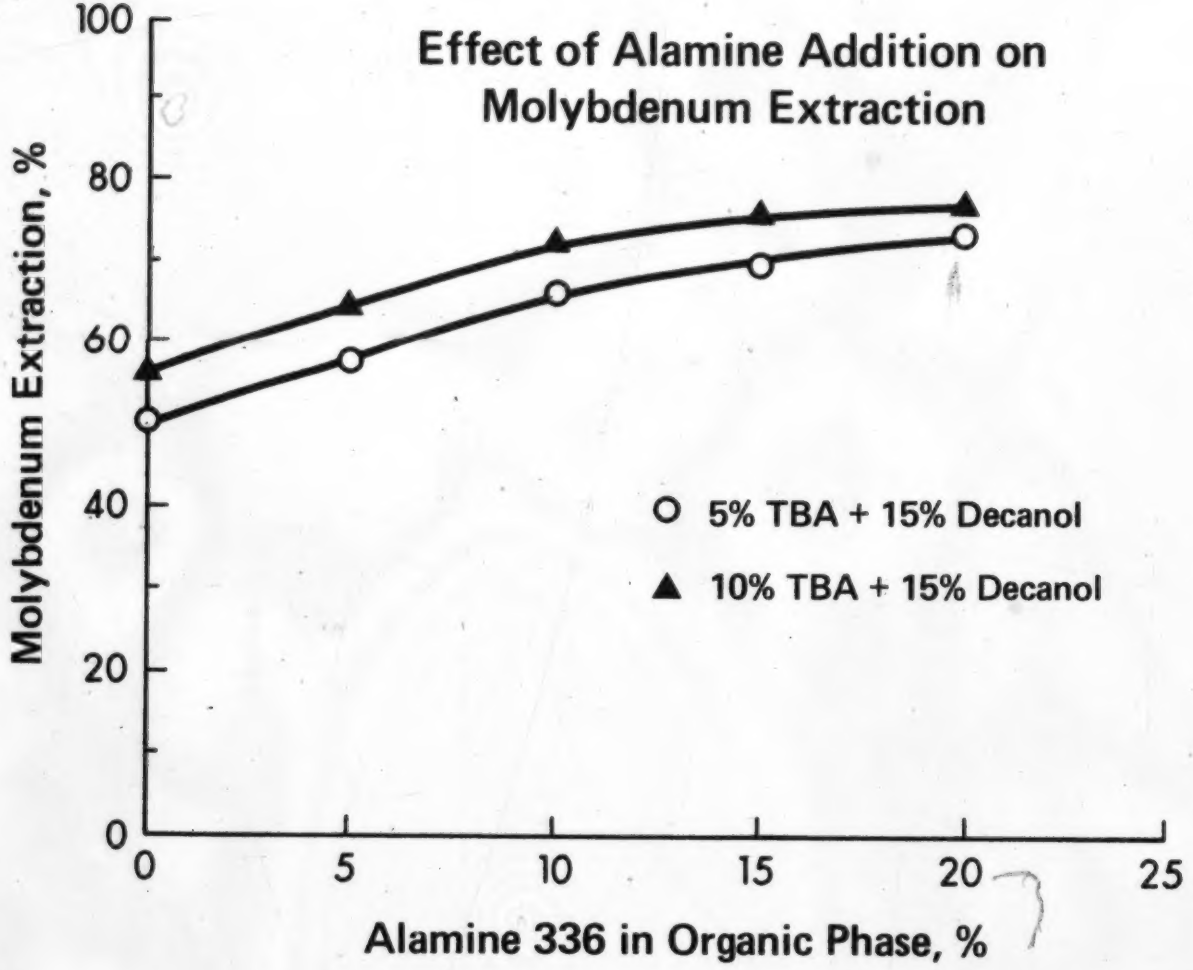


Figure 5 - Dependence of molybdenum extraction on alamine concentration.

optimum organic phase would be calculated on the basis of industrial cost, losses and recovery. In this research, the optimum composition was said to be where the increase in extraction became constant. This criteria gave an optimum composition of 12% alamine and between 5 and 10% tributylamine. As the extraction could be increased by a 1:1 extractant ratio the final composition was evaluated as 12% alamine 336, 10% tributylamine and 15% decanol in kerosene. This 12:10:15 mixture gives approximately a 74% single stage molybdenum extraction and a 7% P_2O_5 extraction.

Figure 6 confirms the quantity of decanol required in a simulated countercurrent test. When numerous fresh aqueous contacts are made to a single organic phase, a three phase system is produced unless the extractant contains 15% decanol.

Reaction Mechanism

The organic phase contains two active extractants, alamine 336 and tributylamine, which will be represented as R_3^1N and $R_3^{11}N$, respectively. The formulae of the two extractants and the modifier, decanol, are shown in Figure 7. The two active components in the aqueous phase are phosphoric acid, H_3PO_4, and a molybdenum species. Molybdenum and phosphorous have the ability of forming a wide

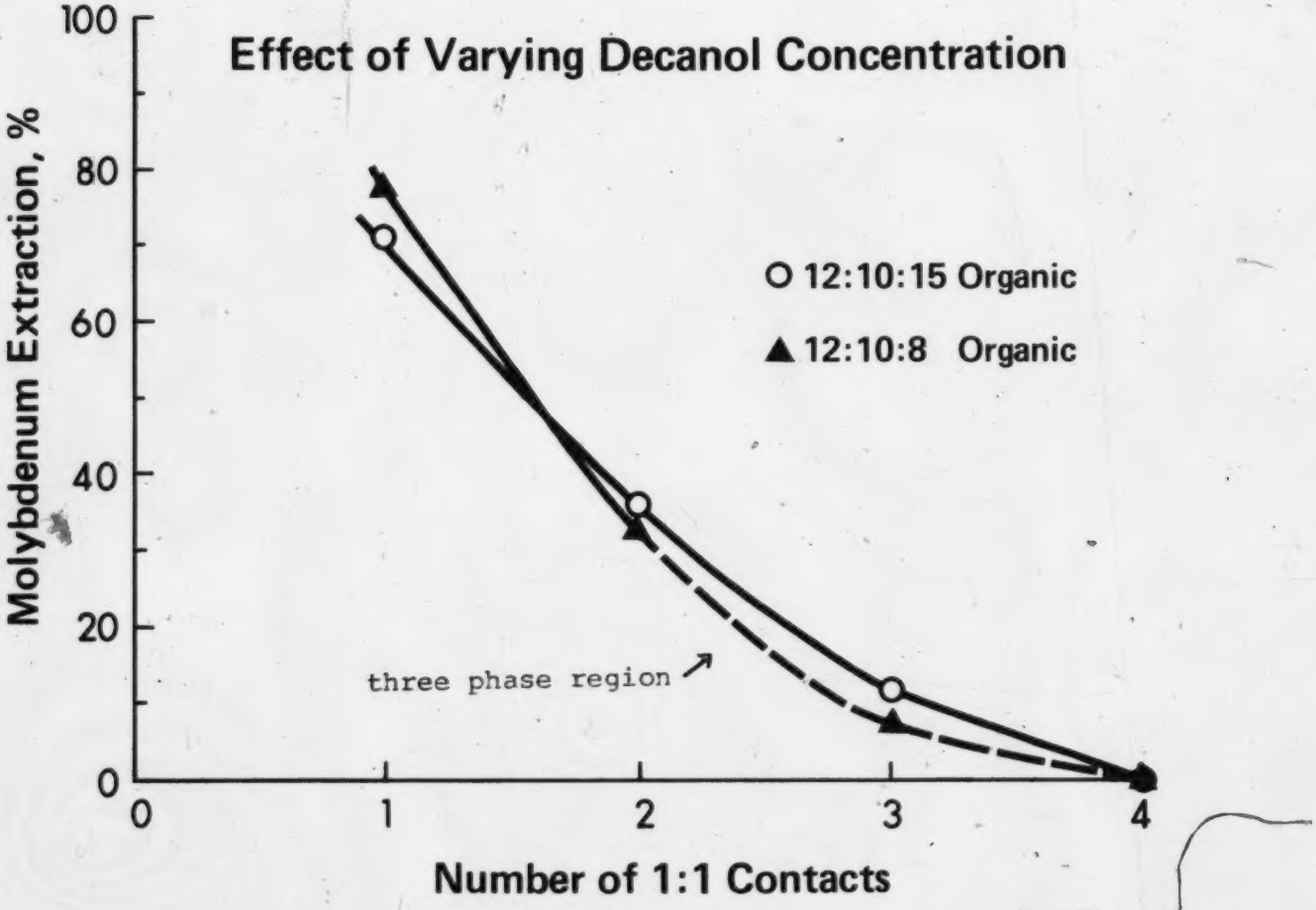
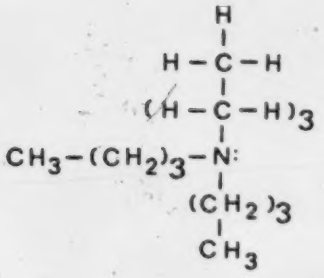
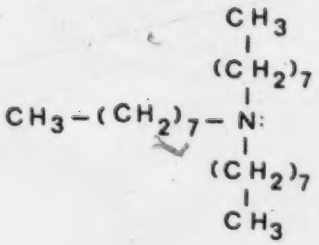


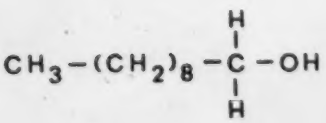
Figure 6 - Effect of repeated aqueous contacts on a single organic phase of composition - 12% alamine, 10% TBA, 8% and 15% decanol.



Tributylamine



Alamine 336



Decanol

Figure 7 - Formulae of tributylamine, alamine and decanol.

range of polymolybdophosphates. Various studies have shown the formation of at least 24 such species, ranging from $H_2P_2MoO_9^{3-}$ to $H_{36}P\,Mo_{12}O_{56}^{6-}$. Furthermore, a series of reversible redox reactions are possible as in Eq. (1), where the oxidation state of molybdenum will change but the ion charge and structure will only slightly vary.

$$P_2Mo_{18}O_{62}^{6-} \underset{}{\overset{2e^-,2H^+}{\rightleftharpoons}} H_2P_2Mo_{18}O_{62}^{6-} \underset{}{\overset{2e^-,2H^+}{\rightleftharpoons}} H_4P_2Mo_{18}O_{62}^{6-} \underset{}{\overset{2e^-,2H^+}{\rightleftharpoons}} H_6P_2Mo_{18}O_{62}^{6-} \qquad (1)$$

Unfortunately, no reports have been located measuring either the ionic constituents in high phosphate concentration solutions, or reliable analytical techniques for determining the ions. So the polymolybdophosphate ion will be represented as $Mo_xP_yO_zH_w^{n-}$.

The general equation for the extraction of molybdenum will be

$$\underline{a\ R_3^{I}N} + \underline{b\ R_3^{II}N} + (Mo_xP_yO_zH_w)^{n-} + nH^+ \rightarrow \underline{(R_3^{I}N)_a\,(R_3^{II}N)_b\,(Mo_xP_yO_zH_{w+n})}\ , \qquad (2)$$

(underlined species are in the organic phase).

The equilibrium constant K_2, Eq. (2), ignoring activity coefficients is

$$K_2 = \frac{[(R_3^{I}N)_a \ (R_3^{II}N)_b \ (Mo_xP_yO_zH_{w+n})]}{\underline{[R_3^{I}N]}^a \ \underline{[R_3^{II}N]}^b \ [Mo_xP_yO_zH_w^{n-}] \ [H^+]^n} \quad (3)$$

Now, $$\frac{[(R_3^{I}N)_a \ (R_3^{II}N)_b \ (Mo_xP_yO_zH_{w+n})]}{[Mo_xP_yO_zH_w^{n-}]} = D_{Mo}$$

where D_{Mo} is the distribution coefficient of molybdenum. Since molybdenum concentration (50 ppm) is so much smaller than the extractant concentration (10-12%) and the acid concentration (5·5M), the $[H^+]$ can be assumed constant and, $\underline{[R_3^{I}N]}$ and $\underline{[R_3^{II}N]}$ remain unchanged by molybdenum extraction. Therefore, Eq. (3) becomes

$$K_2^{1} = \frac{D_{Mo}}{\underline{[R_3^{I}N]}^a \ \underline{[R_3^{II}N]}^b} \quad (4)$$

Taking logarithms, Eq. (4) becomes

$$K_2^{1} = \log D_{Mo} - a \log \underline{[R_3^{I}N]} - b \log \underline{[R_3^{II}N]} \quad (5)$$

Now, if $\underline{[R_3^{I}N]}$ is held constant and $\underline{[R_3^{II}N]}$ is varied, a graphical plot of log D_{Mo} vs. % tributylamine gives a

value for b. A similar plot will produce a value for a. The data needed to obtain these values were presented in Figures 4 and 5. A least squares determination of a and b gave the values shown in Table VIII.

Table VIII - Determination of extractant ratio in extracted molybdenum species.

Organic Phase Alamine	TBA	a	b
5	var.	-	0.475
20	var.	-	0.528
var.	5	0.492	-
var.	10	0.415	-

If we approximate a and b as 0.5, the extraction equation is

$$\underline{0.5R_3^{I}N} + \underline{0.5R_3^{II}N} + (Mo_xP_yO_zH_w)^{n-} + nH^+ + \underline{(R_3^{I}N)_{0.5}\ (R_3^{II}N)_{0.5}\ (Mo_xP_yO_zH_{w+n})} \cdot \quad (6)$$

For phosphoric acid extraction,

$$\underline{e\ R_3^1N} + \underline{e\ R_3^{11}N} + tH_3PO_4 \rightarrow$$

$$\underline{(R_3^1N)_e\ (R_3^{11}N)_e\ (H_3PO_4)_t} \qquad (7)$$

where R_3^1N is alamine 336 $(C_8H_{17})_3N$

$R_3^{11}N$ is tributylamine $(C_4H_9)_3N$.

The value of e appears to be between 1 and 1.5. The determination is limited only by the phosphate determination.

Summary

Allowing for the limitations of the range of extractants studied in a limited time, and no identification of economic requirements, the optimum extractant was found to be 12% alamine 336, 10% tributylamine and 15% decanol in kerosene. The extraction equation was also determined, although the exact nature of the phosphamolybdate species requires further investigation.

VARIABLE EXTRACTION CONDITIONS

Mixing Time

Amine type extractants normally reach equilibrium very quickly; this fact is confirmed by Figure 8. The equilibrium extraction for the 12:10:15 organic is 79%; this value is slightly higher than previously stated on page 28. This increase is caused by using fresh organic solutions which can decay, the amines changing into amine salts.

A ten minute mixing time is suitable to reach extraction equilibrium and the remaining tests will all use a 10 minute mix.

Molybdenum Concentration

The molybdenum concentration in industrial acid varies, depending on the source of the phosphate rock. Figure 9 shows that with an artificial acid solution the extraction remains high up to 500 ppm molybdenum. At this concentration, the organic extractant can remove a concentration of 340 ppm molybdenum if no competing metal species are present in the acid. The absence of any substantial change in the extraction suggests that the molybdophosphate species remains constant as the molybdenum concentration increases from 50 to 500 ppm.

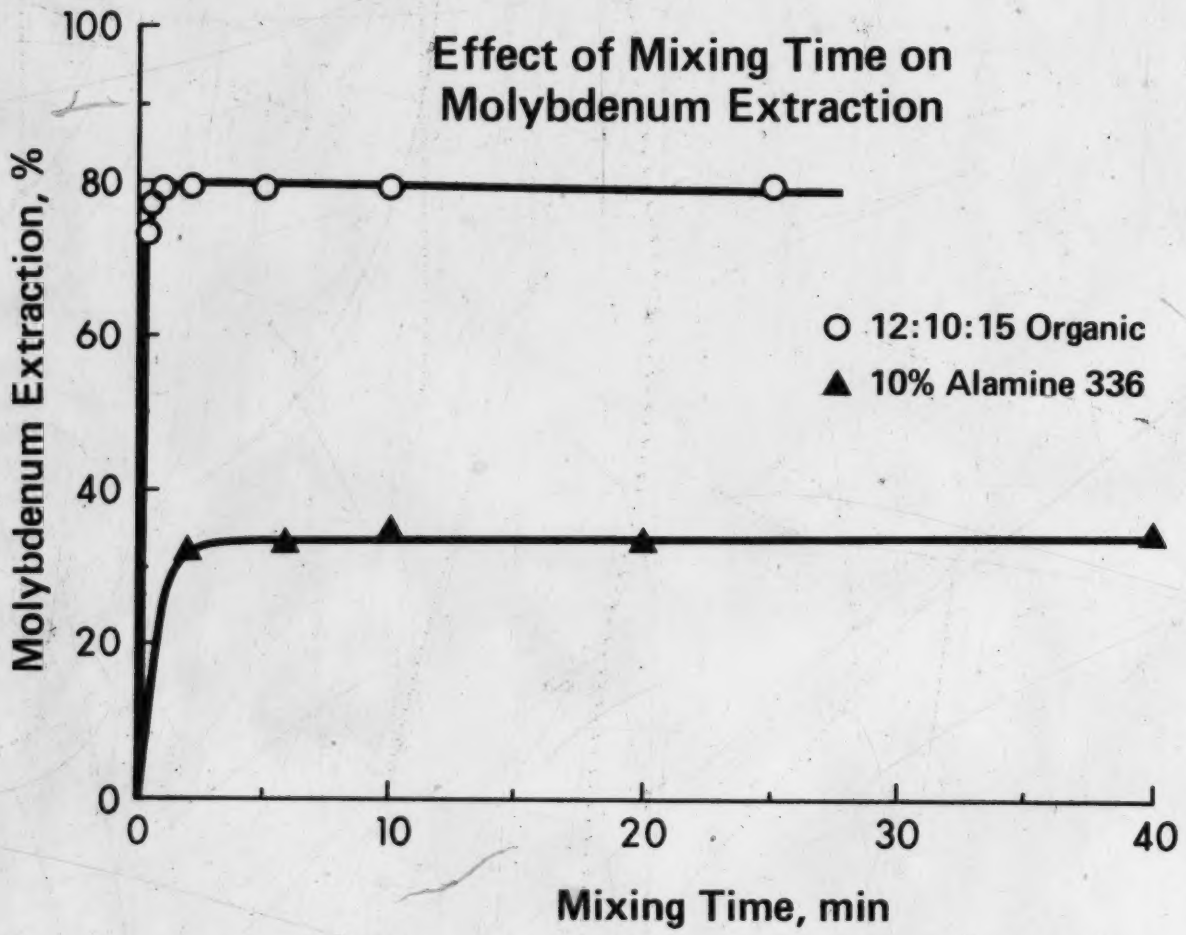


Figure 8 - Dependence of molybdenum extraction on mixing time for 12:10:15 and 10% alamine extractants.

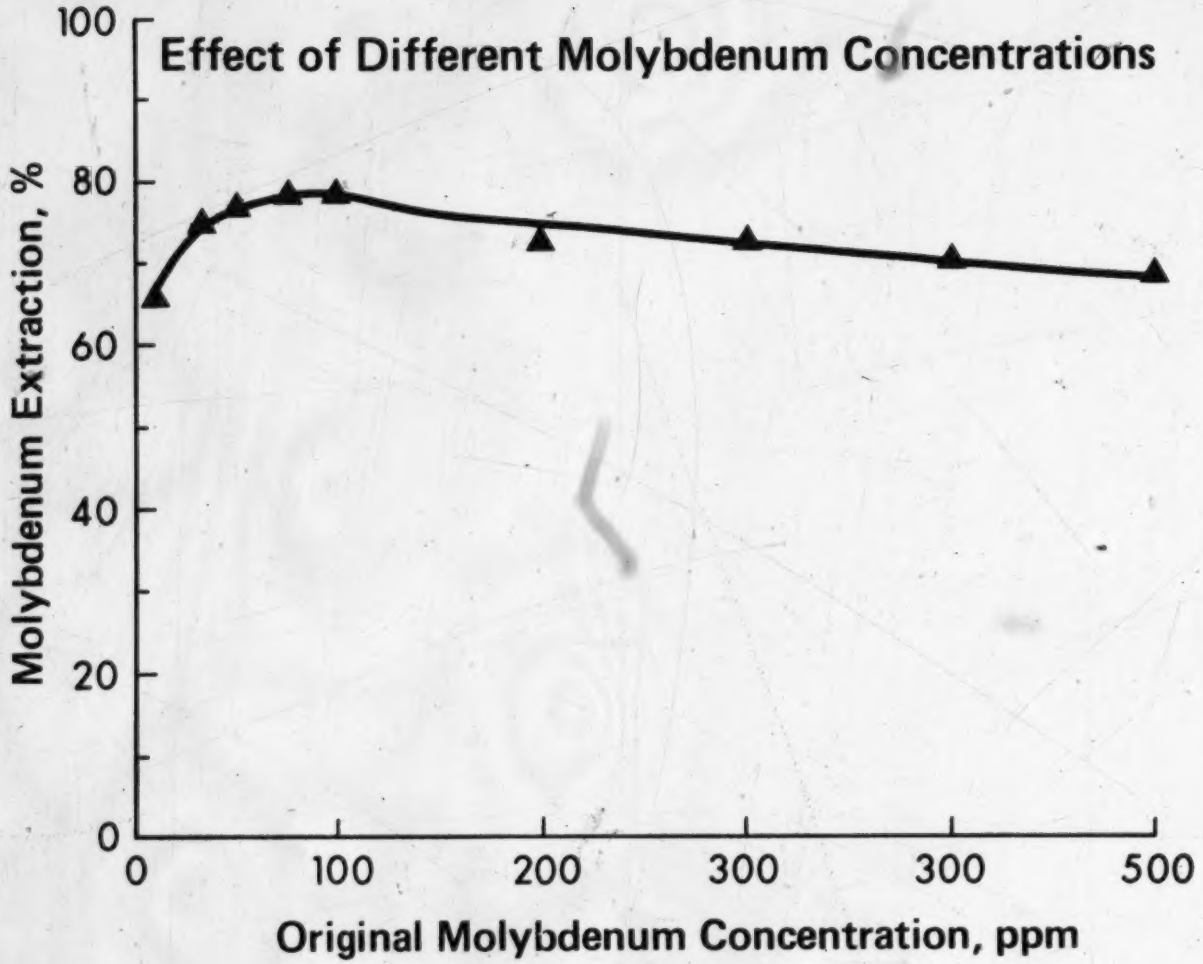


Figure 9 - Effect of different molybdenum concentrations on molybdenum extraction.

Acid Strength

The URC uranium extraction process[4], strips the loaded organic solution with the concentrated 54% P_2O_5 acid process solution, i.e., zero extraction at high acid concentration. Figure 10 shows the variation in molybdenum extraction as the phosphoric acid concentration varies. The decrease in molybdenum extraction as the acid strength increases may be explained by two reasons.

i) The extraction of molybdenum and phosphoric acid are competitive systems. As the acid concentration increases the molybdenum extraction decreases. The reduction in molybdenum extraction is not large enough to produce a noticeable change in P_2O_5 extraction which remains at 6 - 8%.

ii) Variation of acid concentration will alter the molybdophosphate species[29], with a subsequent change in its ability to be extracted.

Above 8M acid a three phase system is formed, caused by a change in polarization due to a change in the nature of the extracted species by either of the above reasons. No reasonable change in acid concentration can produce an industrially useful change in molybdenum extraction.

Temperature

Several routes for the extraction of uranium[11] have used variation of temperature to assist in stripping as shown in Figure 1, page 11. When the temperature of

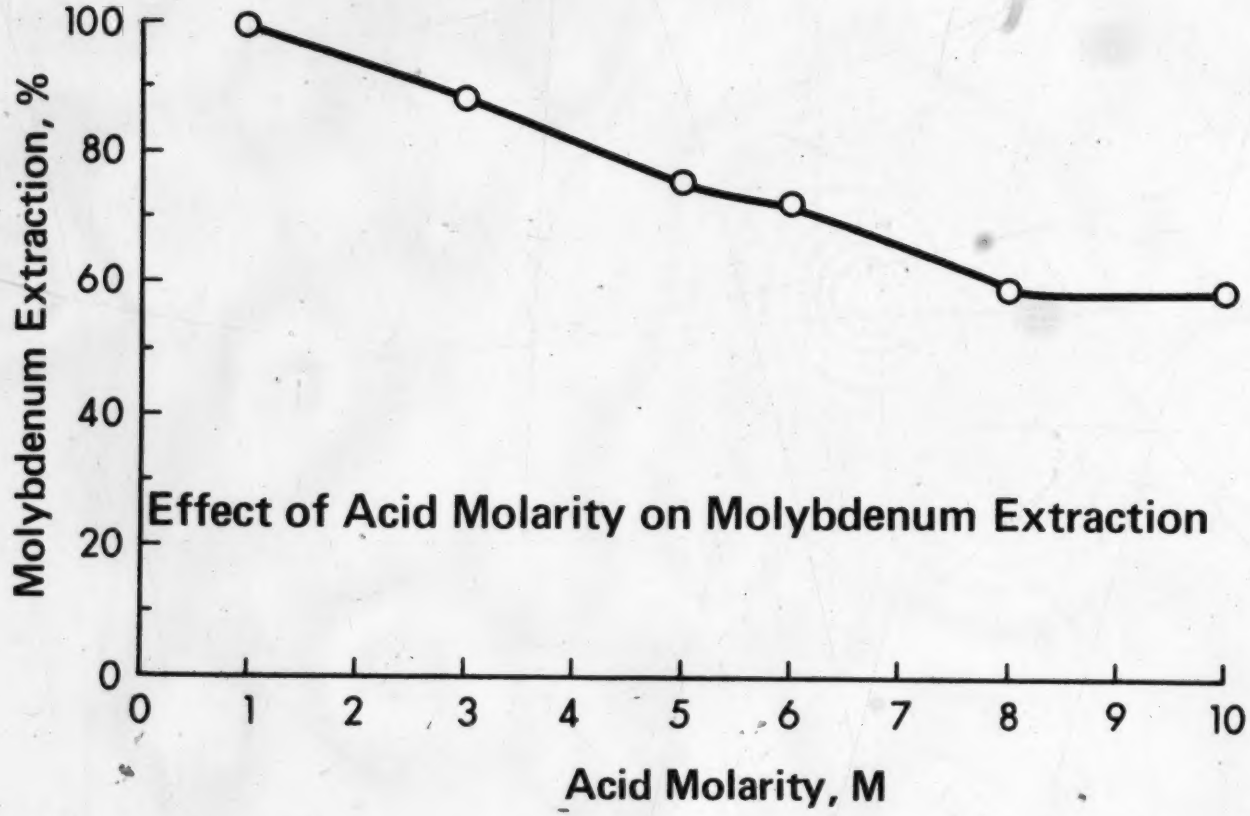


Figure 10 - Variation of molybdenum extraction with H_3PO_4 concentration.

the molybdenum extraction system was varied, the expected decrease in molybdenum extraction was not observed, as shown in Figure 11. As the temperature increased from 25 to 65°C, the P_2O_5 extraction decreased from 7.5% to 2.5%. This decrease produces an extraction increase in the competitive molybdenum system which is nullified by the effect of temperature on molybdenum extraction.

Interfering Species

Alamine type extractants do not extract non-transition group metals[27], so only the major transition metal interferences will be considered.

a. Iron

Iron is the major metal in wet process phosphoric acid with an average concentration of 8 g/l. Figure 12 shows that iron noticeably reduces molybdenum extraction at any iron concentration. However, iron extraction remains constant at 8% when the concentration is varied.

As the molybdenum extraction has been reduced by half, the previously discarded industrial extractants were re-examined with an acid solution containing molybdenum and iron. But as Table IX shows, 12:10:15 extractant is still the most useful.

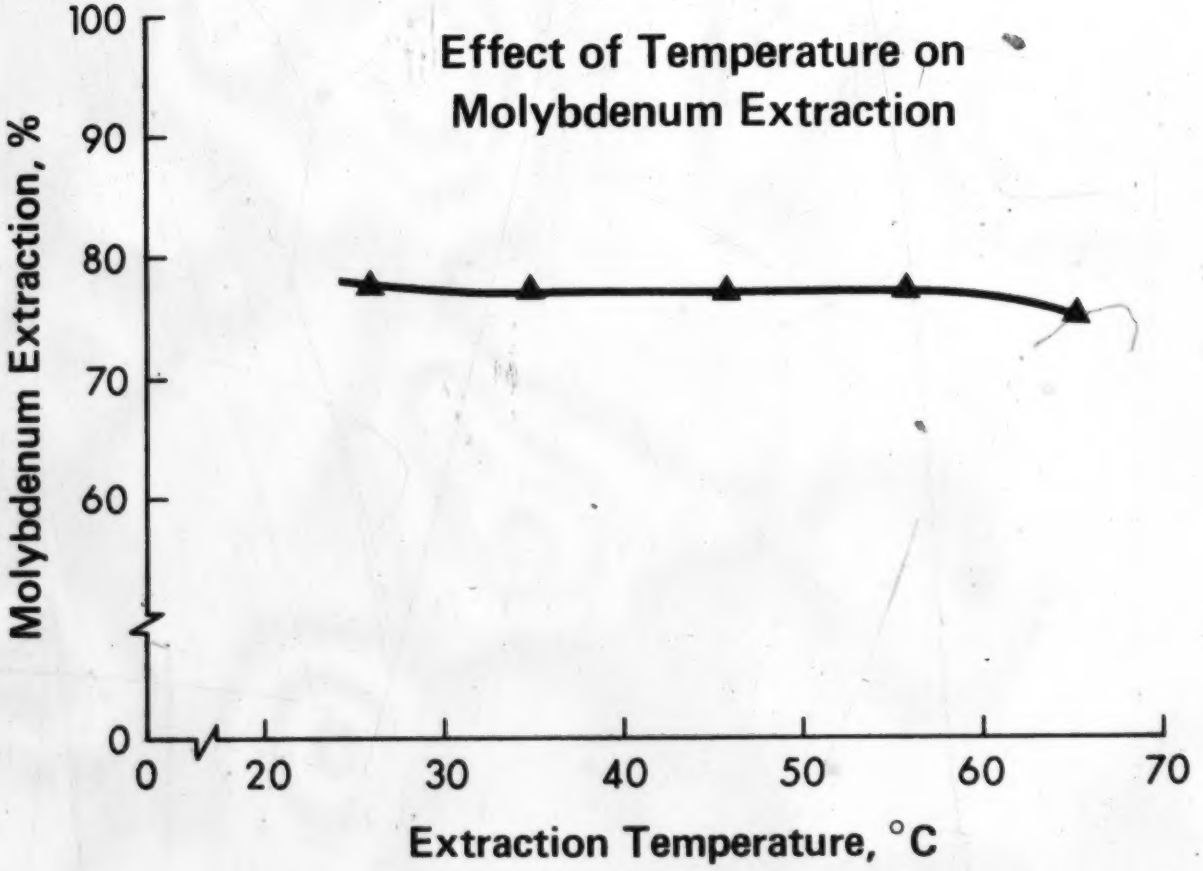


Figure 11 - Effect of temperature on molybdenum extraction.

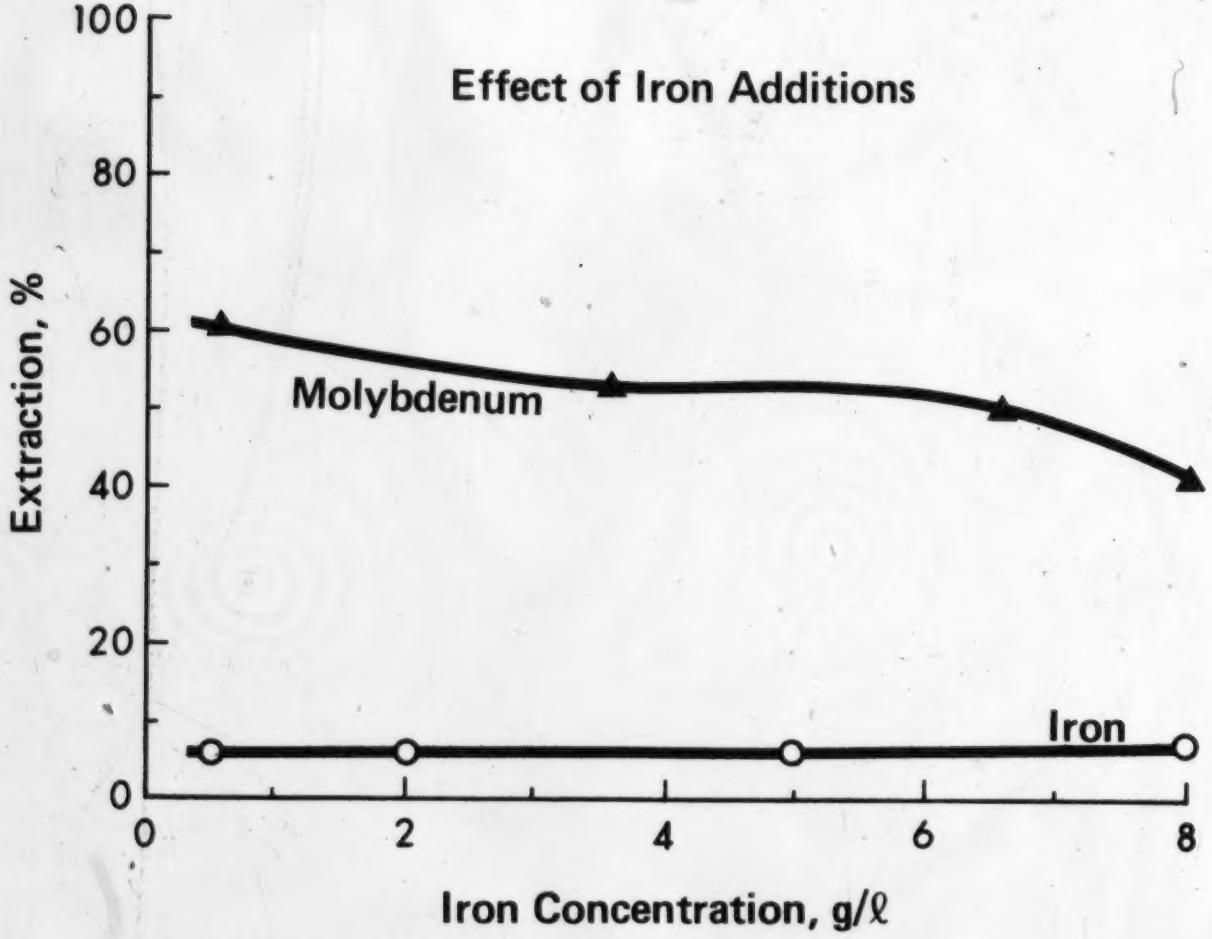


Figure 12 - Metal extractions in systems containing iron and molybdenum.

Table IX - Molybdenum extraction from acid solutions containing 8 g/l iron

Extractant 10% in Kerosene	Molybdenum Extraction, %
Amberlite LA2	9.4
Amberlite LA1	9.4
TOPO	0
Primene JMT	5.5
TBP	11.3
DEHPA	0
Triisoxtylamine	3.8
LIX 70	2.8
Alamine 336	0
12:10:15	41.0
Aliquat 336	9.4

b. Chromium and Vanadium

The chromium and vanadium concentrations can vary widely in wet process acid. Figure 13 shows the effect of chromium and vanadium on molybdenum extraction. Neither metal greatly affects the molybdenum system. It is worth noting that the vanadium extraction varies considerably and that the apparently high chromium extraction observed, does not occur with the industrial acid, c.f. page 49.

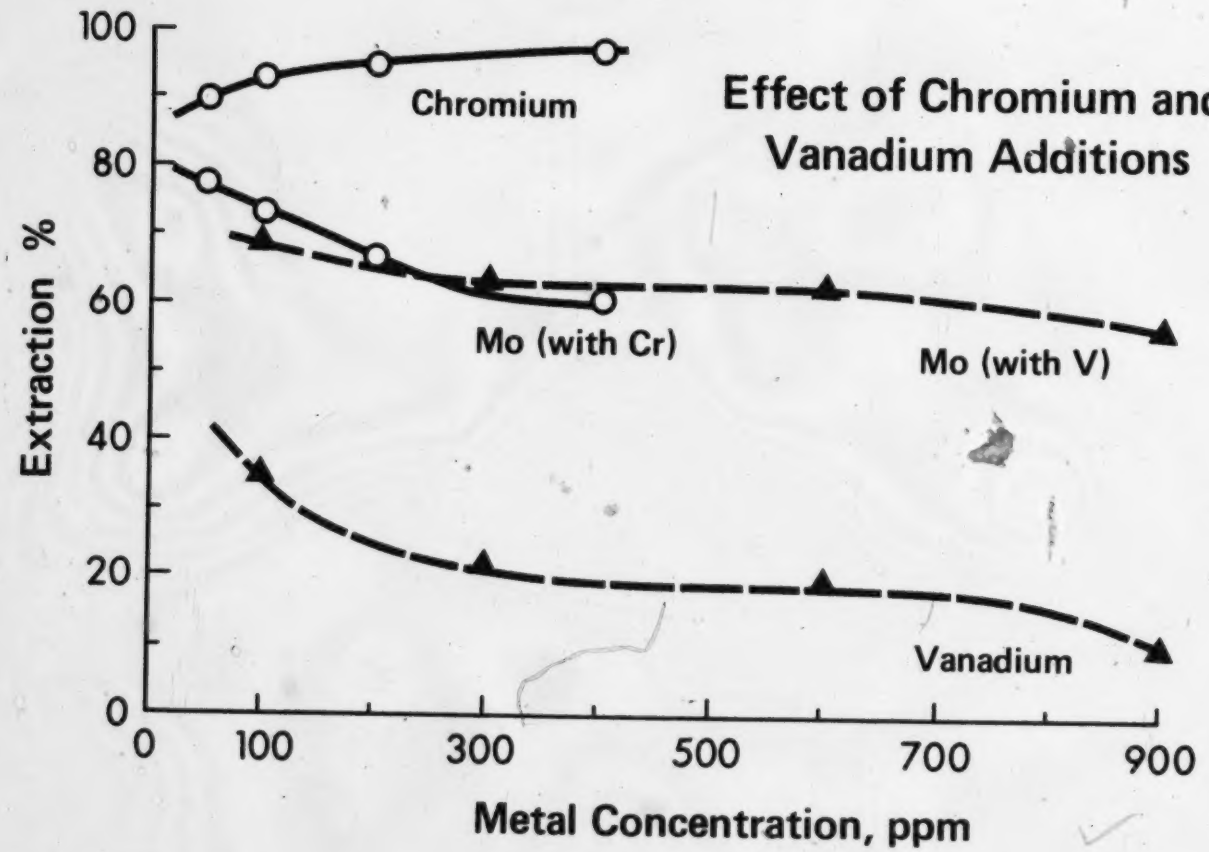


Figure 13 - Metal extractions in systems containing molybdenum, chromium and vanadium.

c. Nickel and Zinc

Neither nickel nor zinc significantly affected molybdenum extraction as shown in Figure 14. The variation in nickel and zinc extraction is difficult to explain, but periodic trends in the transition metals suggest that (Zn or Ni or Ca) - (Fe or Al) - molybdophosphate species may possibly be formed and may affect extraction.

EMF

In the extraction of uranium, Ross[4] notes that the type of extractant to be used and the degree of extraction achieved is dependent on the emf of the phosphoric acid solution. Table X shows the effect of varying emf on molybdenum extraction. The emf of the acid

Table X - Effect of Emf on Molybdenum Extraction

Emf	Molybdenum Extraction, %		
mV	Cr addition	$NaClO_3$ addition	Fe addition
135	60.7	-	41.0
182	60.7	-	51.6
214	72.4	-	54.8
242	-	75.4	64.4
252	-	-	-
293	-	73.8	-
303	-	72.6	-
314	-	72.4	-
320	-	76.7	-

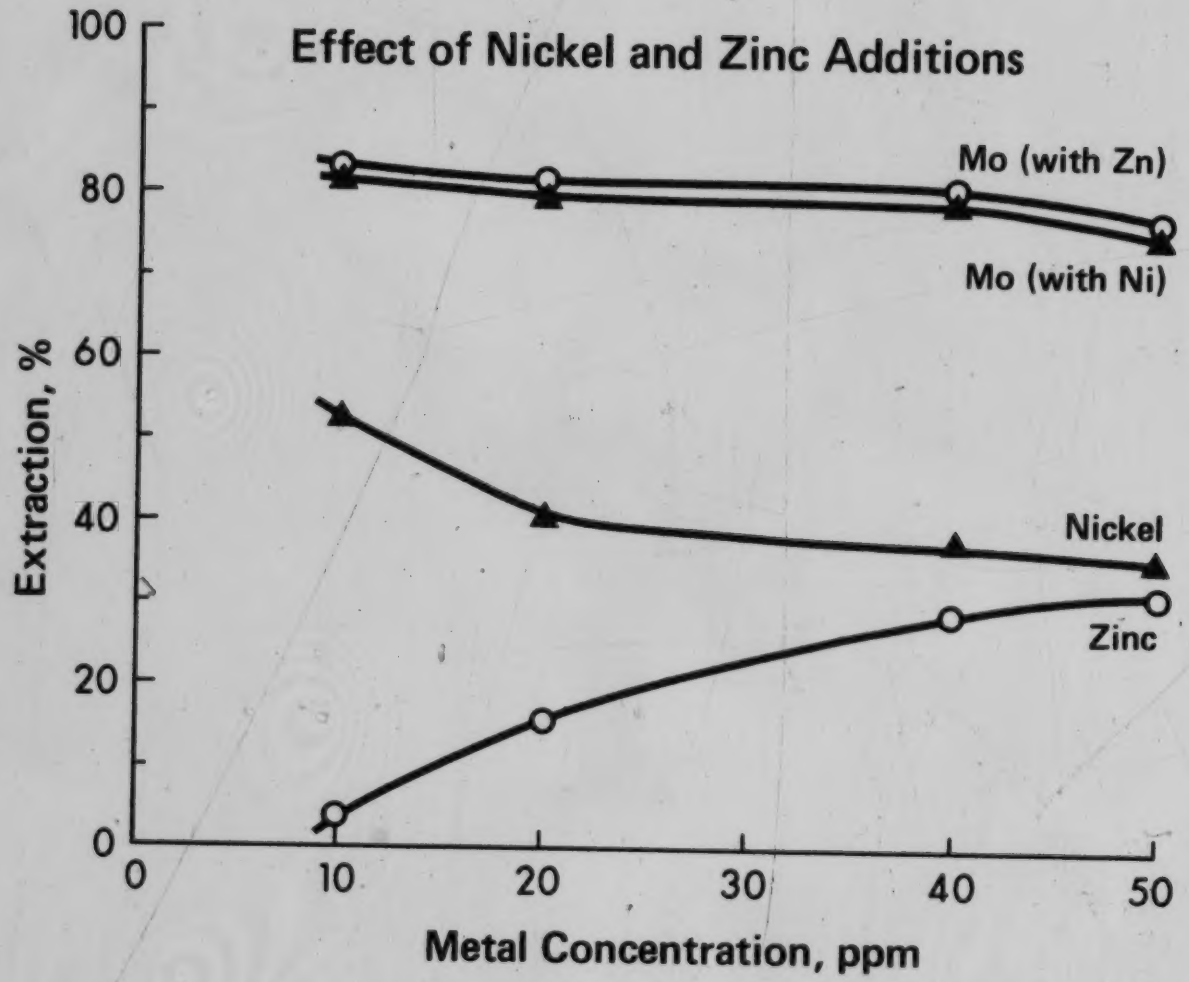


Figure 14 - Metal extractions in systems containing molybdenum, nickel and zinc.

was measured using Ag/AgCl electrode with saturated KCl.

The oxidation of the solution with $NaClO_3$ did not produce any significant change in molybdenum extraction. The reduction of the acid emf using chromium and iron reduced the molybdenum extraction, but to different degrees. The decay in extraction as chromium and iron additions increase, compares favorably to the interference effects of the two metals shown in Fig. 12 and 13.

A change in emf does not have any significant effect on molybdenum extraction. However, the reagent used to change the emf may interfere with the extraction. These results suggest that a reaction similar to Eq. (1) could exist,

$$P_2Mo_{18}O_{62}^{6-} \underset{}{\overset{2e^-,2H^+}{\rightleftharpoons}} H_2P_2Mo_{18}O_{62}^{6-}$$

$$\overset{2e^-,2H^+}{\rightleftharpoons} H_4P_2Mo_{18}O_{62}^{6-} \overset{2e^-,2H^+}{\rightleftharpoons} H_6P_2Mo_{18}O_{62}^{6-}$$

where the extracted species may only slightly vary in its size and charge.

INDUSTRIAL ACID

The industrial wet process phosphoric acid used in the following tests was supplied by Sherritt Gordon Mines Ltd., Fort Saskatchewan, Alberta. It contained the metals concentration shown in Table IV, page 16. A sample of Freeport Chemical Company acid contained 49.9 ppm molybdenum and 439 ppm vanadium. Both acid samples had an emf of 235 mV. The variation of emf in the artificial solutions had little effect on molybdenum extraction, except when an interfering species was used to change the emf. So absence of competing species is more important than solution emf for increasing the extraction.

The 12:10:15 extractant removed 37.8% of the molybdenum, compared to 41% with an $Fe/Mo/P_2O_5$ solution and 77% with a Mo/P_2O_5 solution. In an attempt to increase molybdenum extraction, the industrial acid solution was contacted with the previously discarded extractants. The extraction of molybdenum and the other major metals is shown in Table XI.

This table shows that the 12:10:15 extractant was still the best for molybdenum extraction. It is worth noting that Aliquat 336 extracted over 85% of the zinc, and DEHPA extracted 40% of the chromium and low amounts of the other metals. All the extractants removed 2-5% P_2O_5.

Table XI - Metal extraction with some commercially available extractants

Organic Extractant	Extraction % (industrial acid)					
	Mo	Fe	Zn	Ni	Cr	V
	ppt					
10% Amberlite LA2	13.0	20.7	20.1	13.5	9.8	7.1
10% Amberlite LA1	21.5	9.0	88.8	0	33.9	0
10% Aliquat 336	17.3	27.0	21.8	21.0	43.4	23.2
10% TOPO	21.5	27.0	13.6	13.5	41.4	11.7
10% Primene JMT	16.1	2.3	10.3	22.8	-	14.2
10% TBP	17.3	0.9	18.0	13.0	40.3	15.2
10% DEHPA	30.3	8.1	18.0	9.7	38.1	13.2
10% TOA	13.4	4.4	8.9	13.9	-	8.9
10% LIX 70	37.8	4.2	24.7	29.6	33.6	25.0
12 : 10 : 15 Extractant						

Now that the optimum extractant and extraction conditions have been investigated, the variables associated with an industrial process must be examined.

Phase Ratio

Figure 15 demonstrates the effect on extraction of the phase ratio in a single stage contact. Only the most important constituents are noted: molybdenum, P_2O_5 and iron; the other metal concentrations are reported in Appendix II. Economics must eventually decide the optimum phase ratio, but a 1:1 ratio gives 39% molybdenum extraction while keeping P_2O_5 and iron extraction low. As the extraction of each metal is dependent on the extraction of every other metal it is impossible to simply evaluate the changes in extraction.

Loading

The phase ratio data indicated that reasonable extraction would be achieved if an aqueous aliquot was contacted with three organic portions, e.g., 90% molybdenum extraction at 1:3 phase ratio. So a three stage countercurrent process was simulated with results according to Figure 16 and Table XII. The table also contains a measurement of the selectivity of the extractant for

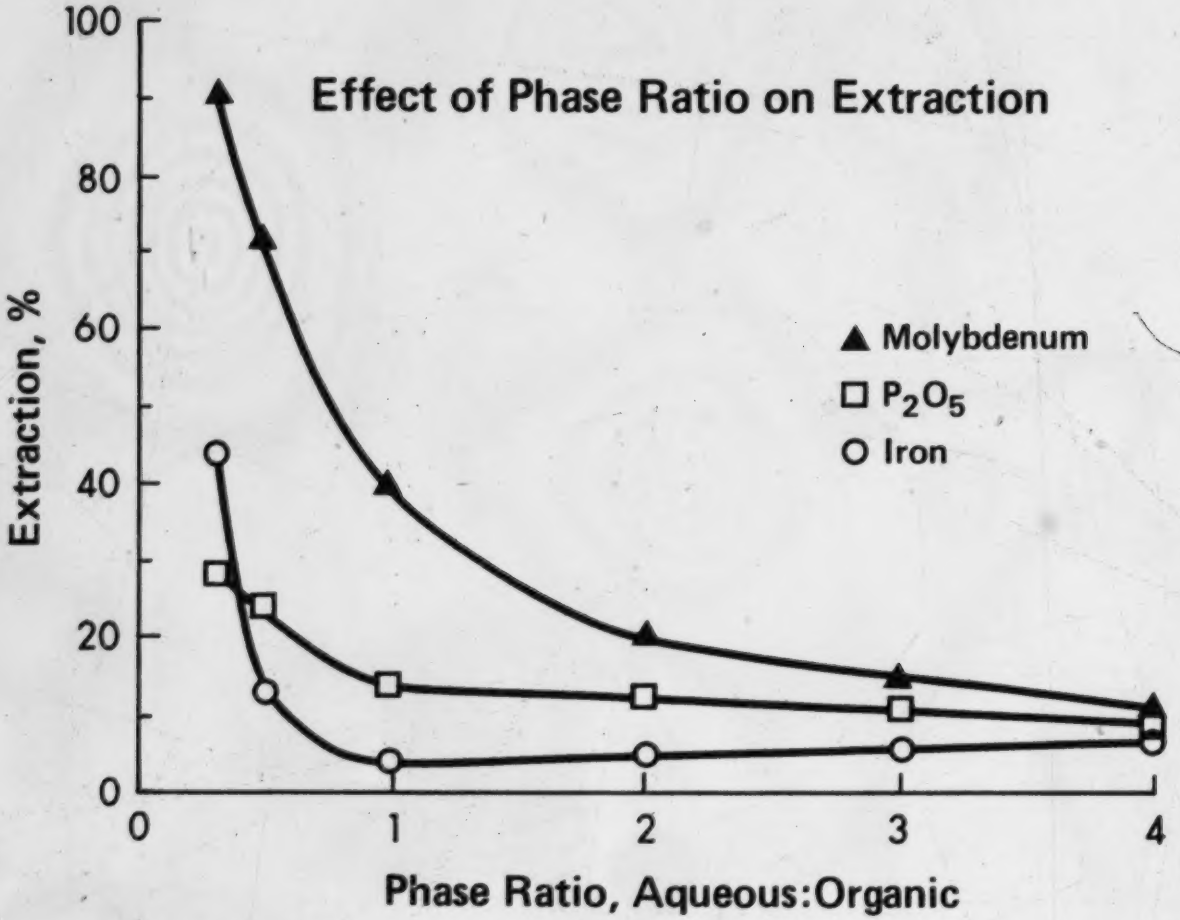


Figure 15 - Effect of phase ratio on Mo, P_2O_5 and Fe extraction.

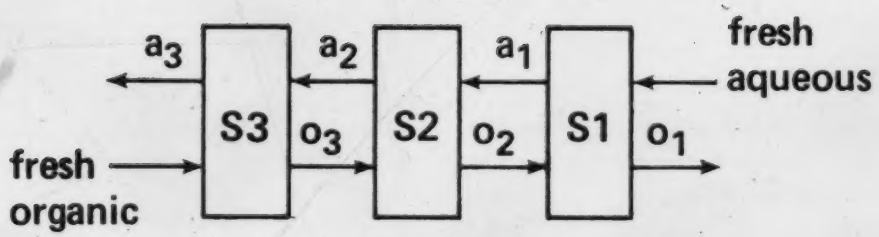


Figure 16 - Simulated 3 stage countercurrent process.

Table XII - Three stage counter current extraction results

Metal	Metal Concentration, ppm						%	
	S1		S2		S3		Overall	Mo
	a_1	o_1	a_2	o_2	a_3	o_3	Extraction	Selectivity
Mo	21.1	44.2	12.7	13.9	7.2	5.5	85.9	1
V	99.4	41.7	78.6	37.1	62.3	16.3	40.1	0.11
Cr	642	318	550	282	360	190	46.9	0.19
Ni	42.3	23.9	39.7	20.4	21.9	17.8	48.2	0.15
Zn	87.9	37.1	77.8	35.5	52.4	23.4	41.5	0.12
Fe	7.8g/l	0.5g/l	7.6g/l	0.3g/l	7.5g/l	0.1g/l	6.7	0.01
P_2O_5	29.5%	5.4%	25.5%	4.9%	24.6%	1.9%	18.0	0.04

molybdenum represented as the ratio of the extraction coefficients of molybdenum and the other metals.

Figure 17 presents the molybdenum results on a McCabe-Thiele extraction curve. The high removal of molybdenum (85.9%) is due to the build-up of phosphate and other extracted metal species in stages 2 and 3 enabling molybdenum to be preferentially extracted in the first stage. This build-up may be due to a change in molybdenum species at low molybdenum concentrations in stages 2 and 3. The lowering of extraction at low molybdenum concentration was also suggested in Figure 9, page 37.

Stripping

Stripping tests were carried out by single extraction steps varying the pH of a 0.5M sulphate solution. Ammonia cannot be used in the stripping operation as it causes the precipitation of ammonium phosphate. The stripping results are shown in Figure 18 and 19.

Iron and chromium can be scrubbed from the organic solution at a pH of 2-3. Molybdenum will have to be removed with the bulk of the nickel, vanadium and zinc. It is possible that zinc and vanadium would reach a constant retained concentration in the organic, without stripping

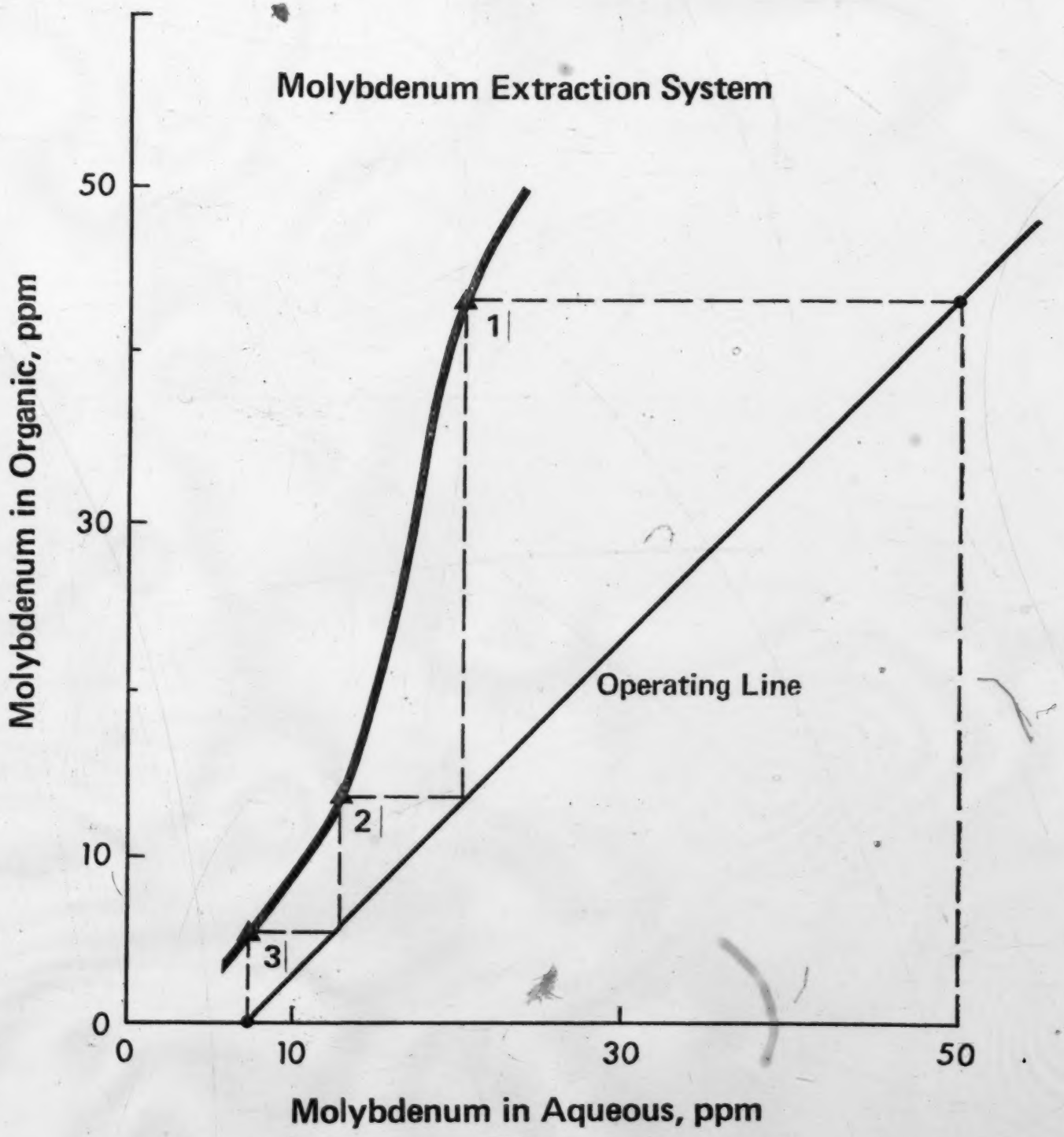


Figure 17 - Countercurrent three-stage molybdenum extraction curve.

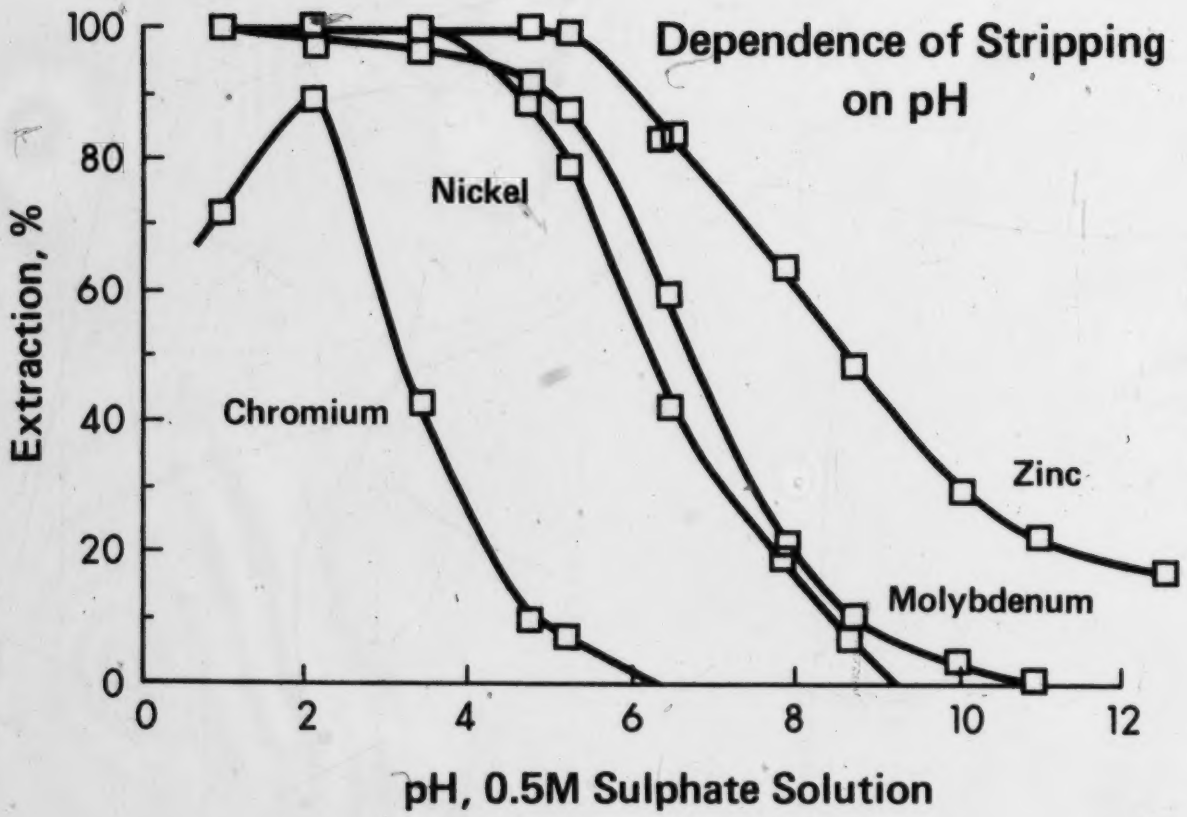


Figure 18 - Effect of pH on the stripping of Mo, Cr, Ni and Zn.

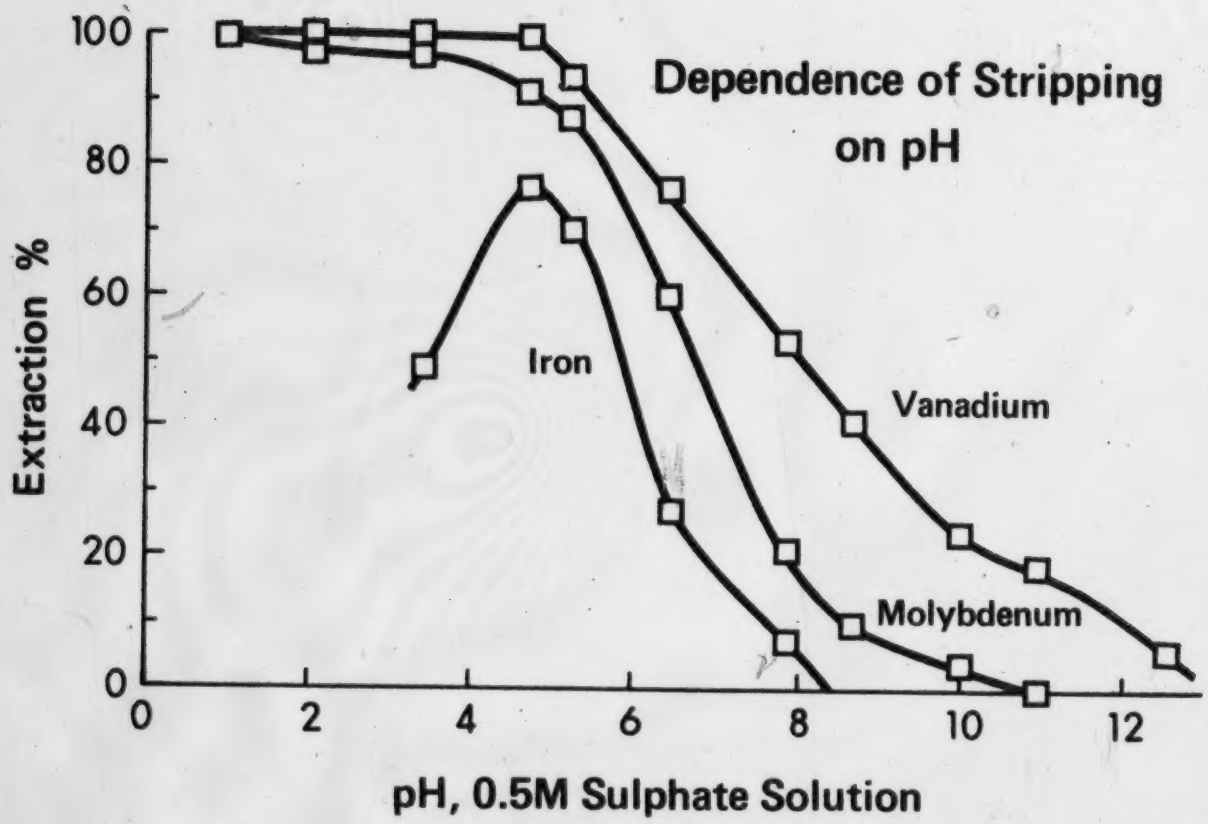


Figure 19 - Effect of pH on the stripping of Mo, Fe and V.

at a high pH. However, zinc in particular may be irreversibly held in the organic without extensive cleaning steps at very high pH.

The resultant solution at a pH of 5, could be treated by a process described by MacInnis, Kim and Laferty[30]. The molybdenum can be extracted by a 15% alamine 336 solution at a constant pH of 5. The organic phase is washed with water and stripped with 15M NH_4OH, easily available in a phosphate plant. The molybdenum loss is negligible (< 0.01%) and ammonium paramolybdate crystals can be produced by evaporation.

ECONOMIC STUDY

To complete this research a brief study of the economics of the process was carried out. It was assumed that a plant processing 200,000 gp day of acid would use the 12:10:15 extractant. The extraction system would consist of a three stage load, a two stage scrub and a two stage strip.

The product solution from five plants could then be collected together and processed by the route described by MacInnis, Kim and Laferty[30], using a 15% alamine 336 solution as the extractant. The recoveries in the two processes would be 80% and 90% respectively, producing approximately 360 lb of ammonium paramolybdate per day.

Preliminary Extraction:

Acid flowrate	-	150 gallons per minute containing 50 ppm molybdenum.
Organic system	-	12% alamine 336, 10% tributylamine and 15% decanol in kerosene.
Equipment	-	3 stage loading, 2 stage scrubbing and 2 stage stripping.
Recovery	-	80% molybdenum recovery with 1/1 loading phase ratio and 5/1 stripping phase ratio.

	Best Case c/lb Mo	Worst Case c/lb Mo
Equipment	51	188
Loading	0.8	1.7
Scrubbing	5.8	7.4
Stripping	2.1	60
Labour and Maintenance	0.8	674
Solvent Loss	15	45
Solvent Treatment	0.3	33
Total	75.8	1009.1

Assuming that the concentrated product solution from five plants can be shipped together and processed by the route previously described[30].

Secondary Extraction:

Acid flowrate - 200,000 gp day containing 0.2 gpl Mo.

Organic system - 15% alamine 336 in kerosene.

Equipment - 2 stage load, 2 stage scrub and 2 stage strip.

Recovery - 90%.

	Best Case c/lb	Worst Case c/lb
Equipment	13	47
Loading	0.2	1.5
Scrubbing	2.2	5.3
Stripping	2.1	15
Labour and Maintenance	0.8	180
Solvent Loss	7.5	15
Solvent Treatment	0.3	33
Total	26.1	296.8

Assumptions:

Equipment with 10 year straight line depreciation.

Solvent Loss at 0.01kg/m^3 of aqueous solution

Ammonium paramolybdate - $2.34 per lb

Tributylamine - $0.68 per lb

Alamine 336 - $1500 per ton (1971)

Decanol - $0.19 per lb

Equipment and processing costs were collected from three sources[31,32,33] and updated to present day prices by the Chemical Engineering price index[34]. The cost of organic solvents and products was obtained from the

Chemical Marketing Reporter[35]. The best case evaluation used maximum solution recycle, lowest equipment costs and no extra labour requirements. The worst case requires high priced equipment, high solution cost and extra labour demands.

The total producing cost varies between $1 and $13 per lb of ammonium paramolybdate which has a current market value of $2.30 per lb. As the cases examined are extremes the probable cost will be in the central price range, $5-10 per lb. These costs ignore any shipping costs and the cost of filtering and drying the final product. A detailed cost study would be required for any prospective operation. Only in the most favorable circumstances, e.g., high molybdenum acid and local markets, would the process appear economically viable.

CONCLUSIONS AND RECOMMENDATIONS

Within the limitations of the number of extractants studied, the optimum extractant for the recovery of molybdenum from some wet process acids appears to be 12% alamine 336, 10% tributylamine and 15% decanol in kerosene. The relative proportions in the organic phase will vary depending upon economic considerations. This organic extractant can remove 85% of the molybdenum from a 'brown' acid in a 3-stage countercurrent process. But the presence of other metals can seriously affect molybdenum extraction, as well as being extracted themselves. Variation of molybdenum concentration, temperature and acid strength have no useful effect upon molybdenum extraction. Correct stripping can produce a solution containing mainly molybdenum, vanadium, zinc and nickel. This solution can be upgraded to produce ammonium paramolybdate by previously described processes.

Although the process appears promising, economically it will be a doubtful situation unless tributylamine is available in industrial quantities. Also, one must consider, in detail, solvent losses, equipment costs, local acid supplies and markets.

However, a detailed investigation of the economics

of a small scale process working with a high molybdenum acid and an available local market, should be made.

Further research should primarily investigate variations in the acid source, hence composition, and the use of other extractants. Namely, the entire range of amine extractants[28] and a wider range of other types of extractants[36].

Excluding molybdenum, the extraction of zinc and chromium with aliquat and DEHPA, respectively, looked very promising. The extraction of a wider range of metals should be examined, including those of low concentration and high value, if a suitable source can be found.

This study concludes that the extraction of molybdenum from wet process acid is chemically feasible using a mixture of liquid anion exchangers; alamine 336 and tributylamine. Further studies should evaluate slight changes to the extractants, mainly tributylamine, and also to study the economics of a possible industrial molybdenum extraction route.

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APPENDIX ONE

ORGANIC EXTRACTANTS

Solvating Reagents - Solv.

Complete or partial replacement of water, in metal co-ordination sphere, by solvent molecules.

Liquid Cation Exchangers - Cat.

$$\underline{(HR)}_2 + M^{2+} \rightleftarrows \underline{MR}_2 + 2H^+$$

Polymerization and solvation of the extracted complex is possible.

Liquid Anion Exchangers - An.

$$\underline{RN}: + HX \rightleftarrows \underline{RNH^+X^-}$$

$$a\underline{RNH^+X^-} + MA_n^{a-} \rightleftarrows \underline{(RNH)_a\ MA_n} + aX^-$$

Hydroximes-Hyd.

$$n\underline{RH} + M^{n+} \rightarrow \underline{MR_n} + nH^+$$

Bidentate Ligands.

Name	Abb.	Formulae	Type	Typical Uses
Primene JMT	JMT	$C_{20}H_{43}NH_2$	An	Fe
Amberlite LA1	LA1	(Lauryl)(triallyl)NH	An	U
Amberlite LA2	LA2	(Lauryl)(trialkyl)NH	An	U, Cd/Zn
Aliquat 336	Aliquat	$(C_8H_{17})_3N\ CH_3Cl$	An	V,Cr,Mo,U,Au/Ag,Cu
Alamine 336	Alamine	$(C_8H_{17})_3N$	An	U,V,W,Fe,Zn,Zr/Hf,Ni/Co
Di-2ethylhexylphosphoric acid	DEHPA	$(C_4H_9 \cdot C_3H_6 \cdot CH_2)_2PO_2H$	Cat	Zn,U,Be,Co
Di-n-propylamine	DNP	$(CH_3CH_2CH_2)_2NH$	An	
Di-2ethylhexylamine	DEHA	$(C_4H_9 \cdot C_3H_6 \cdot CH_2)_2NH$	An	
Di-n-hexylamine	DNH	$[CH_3(CH_2)_5]_2NH$	An	
Didodecylamine	DDD	$[CH_3(CH_2)_{10}CH_2]_2NH$	An	
Hexylamine	Hex	$C_6H_{13}NH_2$	An	
Octylamine	Oct	$C_8H_{17}NH_2$	An	
Trioctylphenyloxide	TOPO	$(C_8H_{17})_3PO$	Solv.	U_3O_8,Fe/Ti
Triisooctylamine	TOA	$(C_8H_{17})_3N$(pure)	An	Co/Ni
Tributylamine	TBA	$(CH_3CH_2CH_2CH_2)_3N$	An	
Tributylphosphate	TBP	$(C_4H_9O)_3PO$	Solv	U_3O_8,Zr/Hf,Zn/Cd
LIX 70N	LIX	complex	Hyd	Cu
Methylamine	MET	CH_2NH_2	An	

APPENDIX TWO

The process diagrams below are representations of a typical phosphate rock processing operation. They are reproduced from the article by Hoppe[4] published in the Engineering and Mining Journal.

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Figure 3	Flotation plant
Figure 4	Wet rock storage, drying and shipping
Figure 8	Sulphuric acid manufacturing
Figure 9	Phosphoric acid manufacturing
Figure 10	Granular triple superphosphate manufacturing
Figure 11	Granular ammoniated phosphate manufacturing

Fig. 1– Washer section

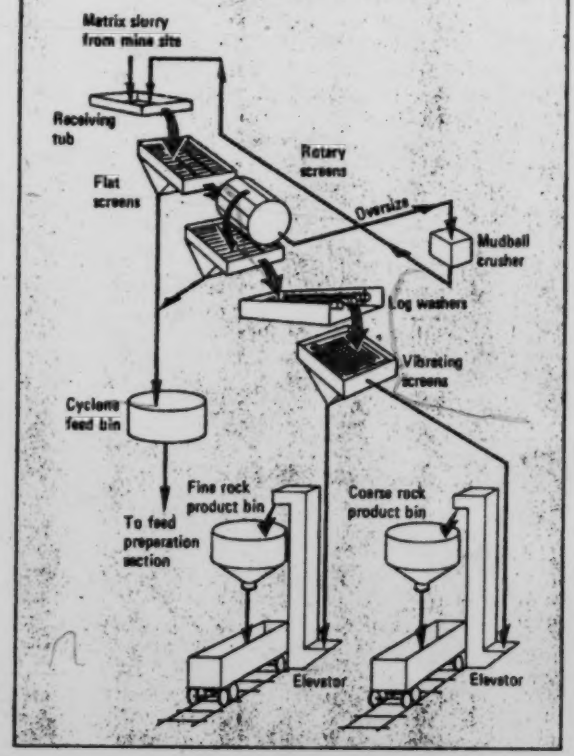


Fig. 2– Feed preparation section

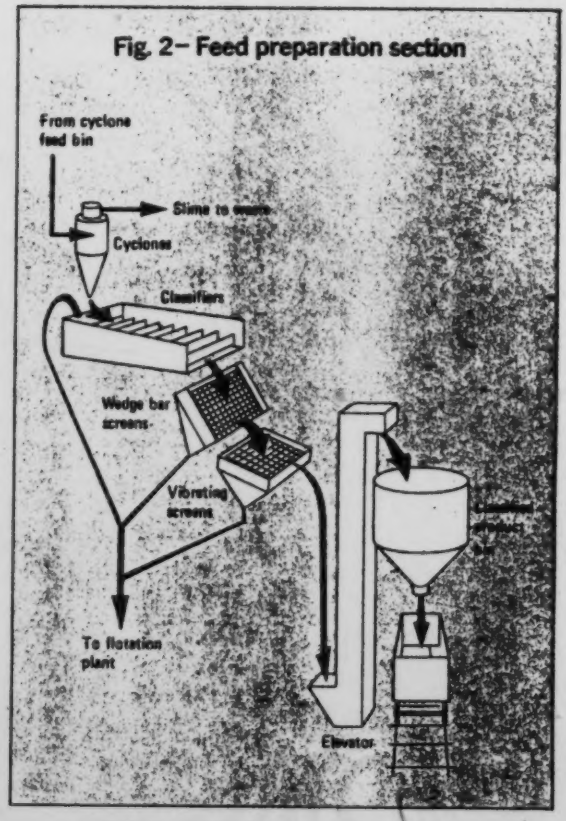


Fig. 3– Flotation plant

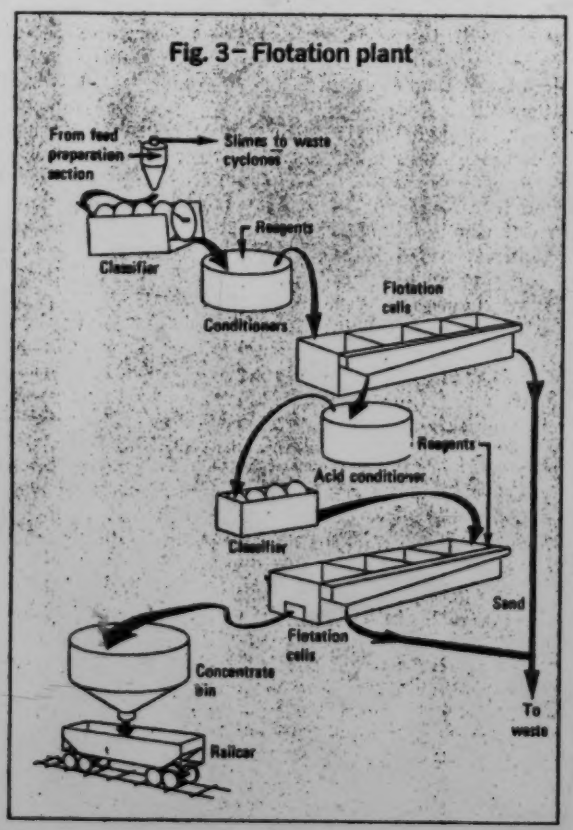


Fig. 4– Wet rock storage, drying, and shipping

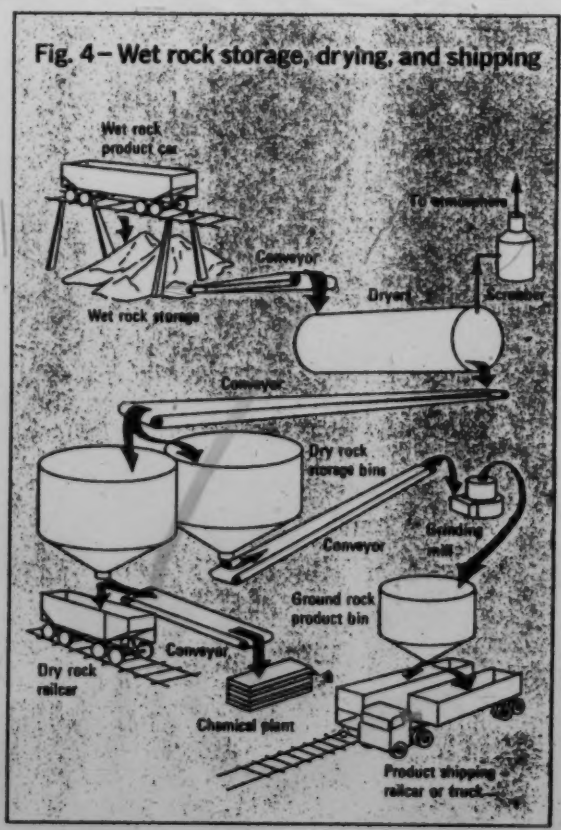


Fig. 8 – Sulphuric acid manufacturing

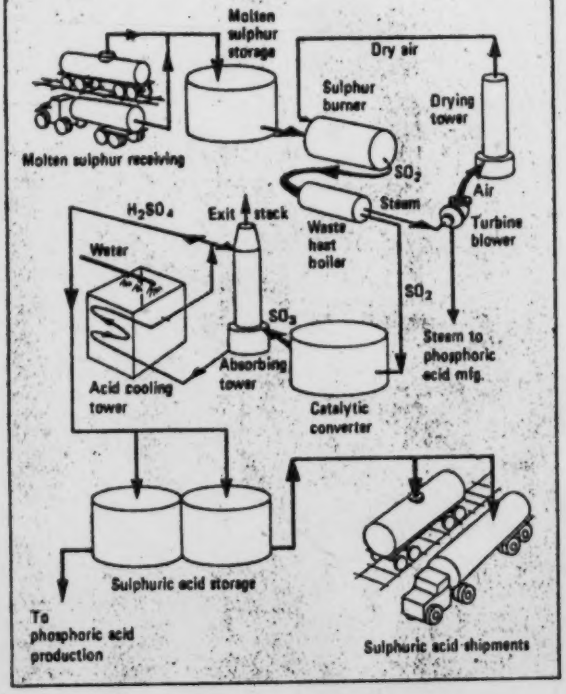


Fig. 9 – Phosphoric acid manufacturing

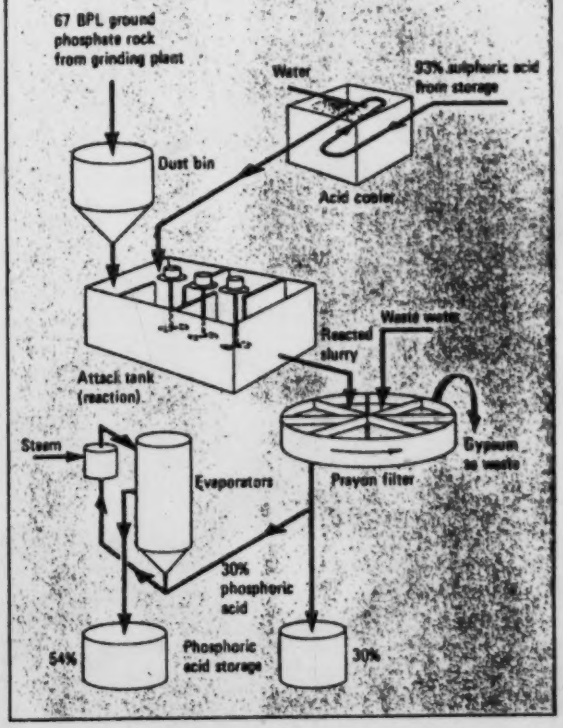


Fig. 10 – Granular triple superphosphate manufacturing

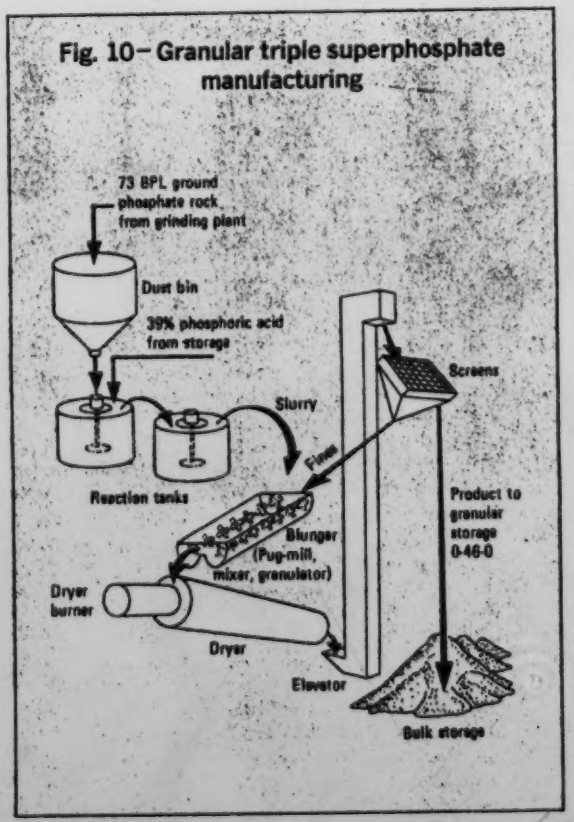
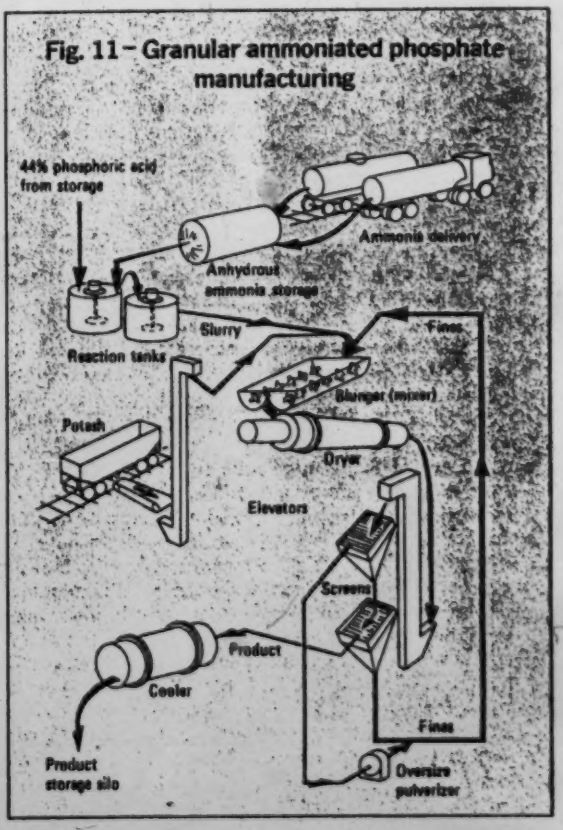


Fig. 11 – Granular ammoniated phosphate manufacturing



APPENDIX THREE

GRAPHICAL DATA

Figure 2 - Analytical Interference Effects

% P_2O_5 v. $\frac{\text{actual concentration}_x}{\text{apparent concentration}_{30}}$ $(\frac{A}{P})$

% P_2O_5	A/P Fe	A/P Mo	A/P Cr,Ni,Zn,V
30	1	1	1
25	1.09	1.20	1.21
20	1.18	1.37	1.39
10	1.34	1.49	1.56
5	1.42	1.51	-

Figure 3 - Effect of Decanol Addition on Molybdenum Extraction

Decanol %	Molybdenum Extraction, % Alamine/TBA	Alamine/DPA
0	75.1 with 3 phases	72.9 with 3 phases
15	72.4 with 2 phases	65.7 with 3 phases
30	66.5 with 2 phases	63.0 with 3 phases

Aqueous - 30% P_2O_5, 50 ppm Mo. Mixing - 15 min.

Phase Ratio - 1:1

Figures 4 & 5 - Effect of TBA and Alamine Addition on Molybdenum Extraction

Aqueous-30% P_2O_5, 50 ppm Mo. Mixing-10 min., 19.5°C

Phase Ratio - 1:1

Alamine %	TBA %	Mo E%	Alamine %	TBA %	Mo E%
5	0	18.0	0	5	51.0
5	5	58.6	5	5	58.0
5	10	65.0	10	5	66.0
5	15	69.5	15	5	69.9
5	20	73.5	20	5	73.4
20	0	54.9	0	10	56.7
20	5	71.5	5	10	65.0
20	10	75.8	10	10	72.3
20	15	80.3	15	10	75.8
20	20	84.2	20	10	76.9
100	0	90.3			

Figure 6 - Effect of Varying Decanol Concentration

Aqueous-30% P_2O_5, 50ppm Mo. Mixing-10 min., 21.2°C

Phase Ratio - 1:1

Contact No.	Mo Extraction, % 12:10:8	12:10:15
1	77.0	71.3
2	33.3	35.6
3	7.4	11.6
4	0	0

Figure 8 - Effect of Mixing Time on Molybdenum Extraction

Mixing Time min.	Molybdenum Extraction % 12:10:15	10% alamine
0.25	73.9	-
0.5	77.1	-
1	79.0	-
2	79.0	32.0
5	79.0	-
6	-	33.0
10	79.0	34.4
20	79.0	33.2
25	79.0	-
40	-	34.4

Aqueous-30% P_2O_5, 51.2 ppm Mo.

Phase Ratio - 1:1. 21°C

Figure 9 - Effect of Different Molybdenum Concentrations

Initial Molybdenum Concentration ppm	Molybdenum Extraction, %
10	66.0
30	75.0
50	76.7
75	78.5
100	78.7
200	72.6
300	72.6
400	69.9
500	68.8

Organic-12:10:15. Aqueous-30% P_2O_5. Mixing-10 min., 21°C

Phase Ratio - 1:1

Figure 10 - Effect of Acid Molarity on Molybdenum Extraction

Acid Molarity M	Molybdenum Extraction %	Phases	Equilibrium pH
0.98	99.0	2	1.19
2.94	88.4	2	0.59
5.00	75.4	2	0.06
5.98	72.4	2	-0.18
8.05	60.7	3	-0.45
10.00	60.7	3	-0.85
30% P_2O_5	75-79	2	-0.15

Organic-12:10:15. Mixing-10 min., 21°C.

Aqueous-50 ppm Mo. Phase Ratio - 1:1

Figure 11 - Effect of Temperature on Molybdenum Extraction

Extraction Temperature °C	Molybdenum Extraction %
25.6	77.7
35.8	77.0
45.9	77.0
55.6	77.0
65.2	75.1

Organic-12:10:15. Mixing-10 min.

Aqueous-30% P_2O_5, 50 ppm Mo. Phase Ratio - 1:1

Figure 12 - Effect of Iron Additions

Fe addition, g/l	Fe extraction, %	Mo extraction, %
8	7.4	41.0
5	6.8	51.0
2	6.3	54.8
0.5	5.9	64.4

Figure 13 - Effect of Chromium and Vanadium Additions

Cr addition, ppm	Cr extraction, %	Mo extraction, %
400	97.5	60.4
200	95.0	66.2
100	93.0	73.8
50	90.0	77.6

V addition, ppm	V extraction, %	Mo extraction, %
900	10.8	57.0
600	19.5	63.4
300	22.0	63.6
100	35.0	68.8

Figure 14 - Effect of Nickel and Zinc Additions

Ni or Zn addition ppm	Extraction, % Ni plus Mo	Extraction, % Zn plus Mo
50	35.0 75.2	30.8 57.0
40	37.5 79.2	28.3 63.4
20	40.0 79.6	15.5 63.3
10	51.9 81.8	3.8 68.8

Figures 12-14: Aqueous-31.5% P_2O_5, 50 ppm Mo.

Phase Ratio- 1:1

Organic-12:10:15. Mixing-10 min., 20.4°C.

Figure 15 - Effect of Phase Ratio on Extraction

Phase Ratio Aq:Org	Percentage Extraction P_2O_5	Mo	Fe	V	Zn	Ni	Cr
4:1	9.6	10.6	6.6	10.3	10.1	7.7	13.1
3:1	11.1	14.7	5.6	13.1	13.2	10.1	16.5
2:1	12.5	20.5	5.2	14.0	16.5	14.9	20.8
1:1	14.9	40.0	4.2	25.0	24.9	29.4	33.6
1:2	24.3	71.7	13.7	46.5	50.8	54.1	51.6
1:3	28.0	90.2	44.2	64.6	50.8	66.6	65.8

Organic-12:10:15. Aqueous - industrial acid.
Mixing-10 min. 21.2°C.

Figure 17 - Molybdenum Extraction System

See Table XII, page 53.

Organic-12:10:15. Aqueous - industrial acid.

Mixing-10 min. 20.3°C. Phase Ratio - 1:1

Figure 18 & 19 - Dependence of Stripping on pH

	% Extraction					
pH	Mo	Fe	Cr	Ni	Zn	V
0.99	100	-	71.5	100	100	100
2.07	97.5	-	89.5	100	100	100
3.43	97.0	49.2	42.7	100	100	100
4.72	91.0	76.3	9.9	88.8	100	99.9
5.25	79.2	70.2	7.1	68.4	99.9	83.4
6.44	59.9	27.1	-	42.7	83.4	76.1
7.87	21.2	7.8	-	19.4	63.6	53.1
8.67	9.7	-	-	8.7	48.2	40.7
10.17	3.4	-	-	-	29.5	23.6
10.96	0.3	-	-	-	22.4	18.8
12.53	-	-	-	-	17.8	6.3

Organic - 3 stage loaded 12:10:15. Phase Ratio-1:1

Aqueous-0.5M sulphate solution. Mixing time-10 min. 20.9°C